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IRON AND STEEL DIVISION

1932

TRANSACTIONS

OF THE

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

Vol. 100

IRON AND STEEL DIVISION 1932

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HELD AT BLUEFIELD, W. VA., OCTOBER, 1931 AND AT NEW YORK, FEBRUARY, 1932

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Notice

This volume is the fifth of a series containing papers and discussions presented before the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers since its organization in 1928; one volume each year, as follows:

1928, Iron and Steel Technology in 1928

1929, 1930, 1931 and 1932, TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Iron and Steel Division

This volume contains papers and discussions presented at the New York Meeting, Feb. 15-18, 1932.

Papers on iron and steel subjects published by the Institute prior to 1928 are to be found in many volumes of the TRANSACTIONS of the Institute; during the past 25 years in Vols. 37 to 45, inclusive; 47, 50 and 51, 53, 56, 58, 62, 67 to 71, inclusive; 73 and 75. Vol. 67 was devoted exclusively to iron and steel.

Iron and steel papers published in the TRANSACTIONS may be found by consulting the general indexes to Vols. 1 to 35 (1871-1904), Vols. 36 to 55 (1905-1916), and Vols. 56 to 72 (1917-1925), and the indexes in succeeding volumes.

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Resumption of Serial Numbers for the Transactions

WITH Volume 99 of the TRANSACTIONS was resumed the serial numbering that was discontinued after the issuance of Volume 76 in 1928. The designation of the present volume therefore is TRANSACTIONS A.I.M.E., Vol. 100, Iron and Steel Division, 1932. The following table shows the existing titles of the volumes published in the interval and also the supplemental designations. Likewise are shown the complete designations of the volumes yet to be issued in 1932. Anyone desiring to revise the designations on the backbones of his volumes can obtain appropriate stickers with gilt letters, to match the binding, at small cost by addressing the office of the Secretary.

PRESENT TITLE OF VOLUME	ADDITIONAL DESIGNATION
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TRANSACTIONS A.I.M.E., Vol. 101, Coal Division, 1932	
TRANSACTIONS A.I.M.E., Vol. 102, General Volume, 1932	

The Howe Memorial Lecture

THE Howe Memorial Lecture was authorized in April, 1923, in memory of Henry Marion Howe, as an annual address to be delivered by invitation under the auspices of the Institute by an individual of recognized and outstanding attainment in the science and practice of iron and steel metallurgy or metallography, chosen by the Board of Directors upon recommendation of the Iron and Steel Division.

So far, only American metallurgists have been invited to deliver the Howe lecture. It is believed that this lecture would gain in importance and significance were it possible to include metallurgists from other countries, but the Institute has not yet been able to do this on account of lack of special funds to support this lectureship.

The titles of the lectures and the lecturers are as follows:

- 1924 What is Steel? By Albert Sauveur.
- 1925 Austenite and Austenitic Steels. By John A. Mathews.
- 1926 Twenty-five Years of Metallography. By William Campbell.
- 1927 Alloy Steels. By Bradley Stoughton.
- 1928 Significance of the Simple Steel Analysis. By Henry D. Hibbard.
- 1929 Studies of Hadfield's Manganese Steel with the High-power Microscope.
By John Howe Hall.
- 1930 The Future of the American Iron and Steel Industry. By Zay Jeffries.
- 1931 On the Art of Metallography. By Francis F. Lucas.
- 1932 On the Rates of Reactions in Solid Steel. By Edgar C. Bain.
- 1933 The lecturer will be George B. Waterhouse; the subject of the lecture,
Steelmaking Processes.

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FOREWORD

THIS volume of the Iron and Steel Division series contains only papers and discussions presented at the annual meeting in February, 1932, instead of both the annual and following fall meetings, as has heretofore been the practice. It is planned that hereafter these volumes will include the material produced at the annual and the preceding fall meetings. By this change the annual volume can be published several months earlier than before.

It has been necessary in the interest of economy this year to publish a smaller volume. The average standard of papers presented was such that the Papers and Publications Committee of the Division had considerable difficulty in holding space down to budget requirements, but it is believed that the papers selected show an unusually high order of merit.

During the past year, the Institute of Metals and the Iron and Steel Divisions jointly sponsored work on gases in metals, and arranged for nine papers on this subject at the February meeting in 1932. In order to continue this work a Gases in Metals Committee was organized at a meeting held May 20, 1932, consisting of: John Johnston, Chairman; J. Tour, Secretary; F. M. Becket, P. H. Brace, M. A. Grossmann, P. D. Merica and S. Skowronski. A round table discussion on Gases in Metals will be scheduled for the February Meeting in 1933.

Cooperative research in the American iron and steel industry is now more generally recognized as the most effective and economical way to work on certain noncompetitive problems of general concern to the whole industry. The work done in this connection under this Division, especially by the Open-hearth Committee, is an outstanding example of the benefit of such cooperation. The study of inclusions in metals by a cooperating group centered at Pittsburgh is another well-known instance of the effectiveness of this type of research. The work planned and carried out on gases in metals is another typical case. As a result of the increased interest in such research, a committee was appointed by Dr. Becket just before he retired from the chairmanship of this Division in February, 1932, to recommend ways and means by which cooperative research could best be promoted in the iron and steel industry.

F. N. SPELLER,

Chairman, Iron and Steel Division, 1932.

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EDGAR C. BAIN
Henry Marion Howe Memorial Lecturer, 1932

On the Rates of Reactions in Solid Steel

BY EDGAR C. BAIN,* KEARNY, N. J.

(Henry Marion Howe Memorial Lecture)†

OF those previously honored as Henry Marion Howe memorial lecturers, several have had the good fortune to know Dr. Howe well, and to work with him; their references to these associations have enriched their lectures. I have not been so favored, nevertheless I should like to acknowledge in a few words the influence upon my thoughts exerted by a brief contact with his personality. In the summer of 1916, Dr. William Campbell, to whom I am so greatly indebted, was patiently imparting sound principles of Metallurgy to a group of which I was an enthusiastic, if somewhat bewildered, member. On an August afternoon Dr. Howe came to our classrooms, and upon Professor Campbell's invitation he spoke informally for some minutes to a few of us. His words may have been a mere greeting, but there was, I felt, something of a challenge in them, and I determined to try to learn more of the fascinating Science of Metallography, of which he and Professor Campbell were masters. During the ensuing months I read his book, "The Metallography of Steel and Cast Iron," just then off the press, in its entirety, and from the pages of that incomparable work I propose to choose a topic for this afternoon's discussion.

While Dr. Howe's final book is clearly an appropriate source of a subject for this memorial address, it has repeatedly occurred to me that one would be hard-pressed to select a topic of any broad significance in the field of iron and steel metallurgy which had not, at one time or another, fruitfully engaged his attention. Accordingly, I shall quote a few sentences from "The Metallography of Steel and Cast Iron" which have determined not only my viewpoint in the preparation of this paper for this occasion, but also the viewpoint maintained in carrying out the experimental work herein reported. To quote:

What is the phase rule? What is it about, and why is it of importance to metallurgists? Today the chief motive for telling readers something about it is to put them on their guard against many of the current attempts to apply it. It is a most remarkable and valuable generalization; its conceptions help greatly toward getting a broad outlook on metallography; but its misconception has brought out a flood of obscuring writings. It tells us about the constitution toward which alloys tend, that which they reach when equilibrium is complete, when all tendencies have asserted them-

* Metallurgist, Research Laboratory, United States Steel Corporation.

† Presented at the New York Meeting, February, 1932. Ninth annual lecture.

selves and have been complied with completely. But it tells us nothing directly about the intermediate stages through which those alloys pass in their attempt to reach that equilibrium, nothing about alloys which are out of equilibrium. And whatever it may teach us indirectly about such inequilibrium is so hedged about with the direct and indirect results of that inequilibrium that its application to any individual case is fraught with the greatest difficulty.

A hasty reading of the phase rule has led to a mass of attempts to apply it to conditions to which it is in its nature inapplicable, *e. g.*, to the constitution of hardened steel, which is evidently very far out of equilibrium. But this is like determining density with a telescope or area with a tuning fork; it is like the mad tea party at which the butter put into the works of the watch was the best butter. If the reader learns no more than to beware of attempts to decipher the conditions of inequilibrium by a law which touches only the conditions of exact equilibrium, if he rejects summarily all attempts to deduce the constitution of hardened steel by the application of the phase rule unless they show a complete mastery of the subject, he will have learned something of value.

The situation has probably changed very little since Howe wrote these entertaining and—I venture to surmise—comforting words, for clearly the physical metallurgist has little need to deal with the mere concise Phase Rule. At the time of the first widespread appreciation of the Gibbs generalization, scientists were not so much interested in the amazingly simple relationship between the number of components and the number of phases in a system under variously restricted conditions as in the brilliant and satisfying concept of the nature of constitutional equilibrium. Similarly today, I venture to believe, we find Howe's appraisal of the definite real value of the phase rule confirmed by our daily experiences. However that may be, the metallurgist will scarcely be able to disregard the implications of the phase rule, since an important part of his accumulated knowledge, a tool of his trade in fact, comprises a vast number of equilibrium diagrams. This convenient graphic representation of fundamental alloy behaviors is, after all, merely a universal convention for presenting the constitution of alloys at various temperatures after all tendencies toward change of crystalline form have asserted themselves. That some of the diagrams so designated are possibly not this precisely does not lessen their importance as a whole.

INTRODUCTION

Among the familiar steels there is no dearth of examples of alloys wherein a change of constituency accompanies a change in temperature, although most pure metals and a number of solid solution alloys have not thus far evinced any tendency toward change in crystalline form when heated or cooled between the freezing point and the lowest temperatures usually secured. A number of alloys, ferrous and nonferrous, which are most serviceable to the engineer are those which undergo a marked change in constitution with change in temperature, and which possess a variety of properties corresponding to the variety of assumable structures. Now

if these changes in the structure of a metal always occurred infallibly and instantly as it is heated and cooled through its characteristic transformation range, metal would in general be fabricated at one temperature and used at another, and there would be little to complicate the art of metal working. But instead, each structural change in the main progresses at a finite rate and this rate varies with the temperature at which the metal is maintained for the transformation; the new constituents once formed as minute crystallites coalesce or grow in particle size at rates also dependent upon temperature; and as a result we must manufacture metal articles according to the exacting schedules of the Art and Science of Heat Treatment. Indeed we are apparently bound to slave under the stern mandates of both Time and Temperature if we would utilize the metals economically.

In general the reactions which occur upon cooling, but which may be suppressed by a very rapid cooling to a temperature very far below the normal transformation range, are most easily observed, for the reaction may be inaugurated at will, interrupted, and again resumed by appropriate cooling or warming over the proper subcritical range. In some of the steels, a structure at elevated temperature may, by rapid cooling, be surprised into missing entirely its opportunity to transform until it is so cold that it has largely lost all inclination to respond to the urge toward equilibrium. For a study of transformation such steels are particularly interesting.

Referring again to the paragraphs quoted earlier from Dr. Howe, we read "It (the phase rule) tells us nothing directly about the intermediate stages through which these alloys pass in their attempt to reach that equilibrium," and I propose to make that sentence serve as a text, mainly for the reason that for us the study of these "intermediate stages" has been vastly more entertaining, on the whole, than the estimation of the constituents which result when the forces tending to rearrange the crystalline architecture of the metal have asserted themselves. That the route along which one travels may be more attractive than the destination I hope may be admitted as a possibility at least, for I shall presume this afternoon to try to interest you, if not in the microscopic scenery along the route to equilibrium, then perhaps in the readings of our speedometer and our mileage recorder, for we shall find, to abandon the metaphor, a rather large variation in speed of reaction, depending upon the type of alloy which is being observed and upon the temperature level at which the steel is transforming. It may well be that not all of these metallurgical reactions, the study of which has kept your speaker from worse metallurgical mischief, have any industrial significance, except in that they should surely be controlled in the ordinary heat treatment of steel. However, if they should be found entertaining or a little amusing, then perhaps an hour of a busy week of serious papers may not have been

spent too wastefully; and I should like to believe, as I read some of Dr. Howe's writing, that he would not have been wholly disinclined toward a chat about the idiosyncrasies of some of our steels even though tomorrow finds the quotations on steel stocks essentially unaffected by all we shall have said.

The period required for achieving equilibrium in many liquid systems is well known and the change in rate, as the reaction proceeds, follows certain fixed rules, and for these a complete epistemology is universally accepted. It is familiar to all of us, how accurately the progress of the reactions between a photographic emulsion and a developer may be predicted. Concerning reactions in the solid, however, much less is known and the velocity often varies in a manner which has not appeared very simple upon the basis of any analysis yet applied.

For our brief contemplation of reaction rates in solid steel I have selected a few which were particularly entertaining to our laboratory. They have to do with

1. The transformation of austenite to ferrite and carbide,
2. The formation of graphite,
3. The diffusion of carbon in austenite and ferrite.

If the impression should be gathered that the various steels are fundamentally similar rather than dissimilar—that they differ one from another chiefly in respect to their rates of reaction—I shall by no means be disappointed, for that view is one to which I have gradually been led.

ESTIMATING THE EXTENT OF AUSTENITE TRANSFORMATION

The first of these, a reaction of some importance certainly in steel technology, is the transformation of austenite to ferrite and carbide. This reaction is possible whenever a portion of steel first heated to form a solid solution of the carbon in gamma iron, and hence austenitic, is permitted to cool to a temperature below that at which the austenite ceases to be really stable. In the case of ordinary steels in process, this opportunity is offered after each heating. Fortunately, for purposes of study as well as for the engineer's uses, this reaction, austenite to ferrite plus carbide, does not get well under way as soon as the temperature of the austenite is suitably depressed. Instead the austenite hesitates for a little time before beginning its transformation. Accordingly, it is possible, by quenching the austenitic metal into a sufficiently effective medium, to cool the whole of a small specimen of steel to almost any desired temperature before the reaction which will form ferrite and carbide has measurably proceeded. The progress of this reaction at a constant temperature may then be studied by any means which at any instant differentiates between the unchanged austenite and its decomposition products. The microscopic examination of specimens quenched after successively longer intervals provides a means of following the reac-

tion; or continuous dilatometric readings are equally satisfactory, except possibly, when the product is the hard martensite. Both of these methods have been employed in the studies to be described and, checked one against the other, appear to be in satisfactory agreement.

RETARDING THE TRANSFORMATION

In some earlier studies, Mr. Davenport and I observed that, for the plain carbon and low-alloy steels, this reaction proceeds with maximum rapidity in the general vicinity of 600°C. to 500°C. (1110°F. to 930°F.) and that in this temperature range a few seconds suffice to permit the austenite to transform wholly to the nodular fine-pearlite type of ferrite-carbide association. It became apparent that in hardening steel the sole task of a commercial quenching medium is to abstract heat from steel with rapidity sufficient to prevent this rapid reaction, and to cool the austenite unchanged through this temperature zone into temperature ranges wherein the harder constituents are formed. Thus indirectly, only, does the rate of cooling affect the hardening of steel. Similarly, it became apparent that the real function of alloying elements which induce deep hardening is merely that of slowing up the reaction in the temperature range of maximum rapidity, namely the 600°C. to 500°C. (1110°F. to 930°F.) zone. It would appear, therefore, useful to ascertain the relative effectiveness of different alloying elements in reducing the rate of austenite transformation at a temperature in this range, and particularly to ascertain the general trend of the effect of increasing amounts of the retarding alloy element. Some estimations of the effectiveness of alloy additions are here presented, as manifested by the rates of transformation in the active temperature zone.

Fig. 1 shows schematically the time required for transformation of austenite (black) to ferrite and carbide (white) in the general case of ordinary low-alloy steels of approximate eutectoid composition; the high rate of reaction at temperatures in the vicinity of 550°C. (1020°F.) is clearly indicated. For an example of the retarding action of increasing

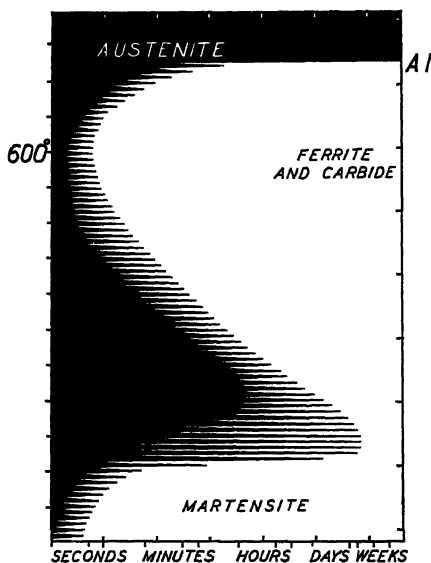
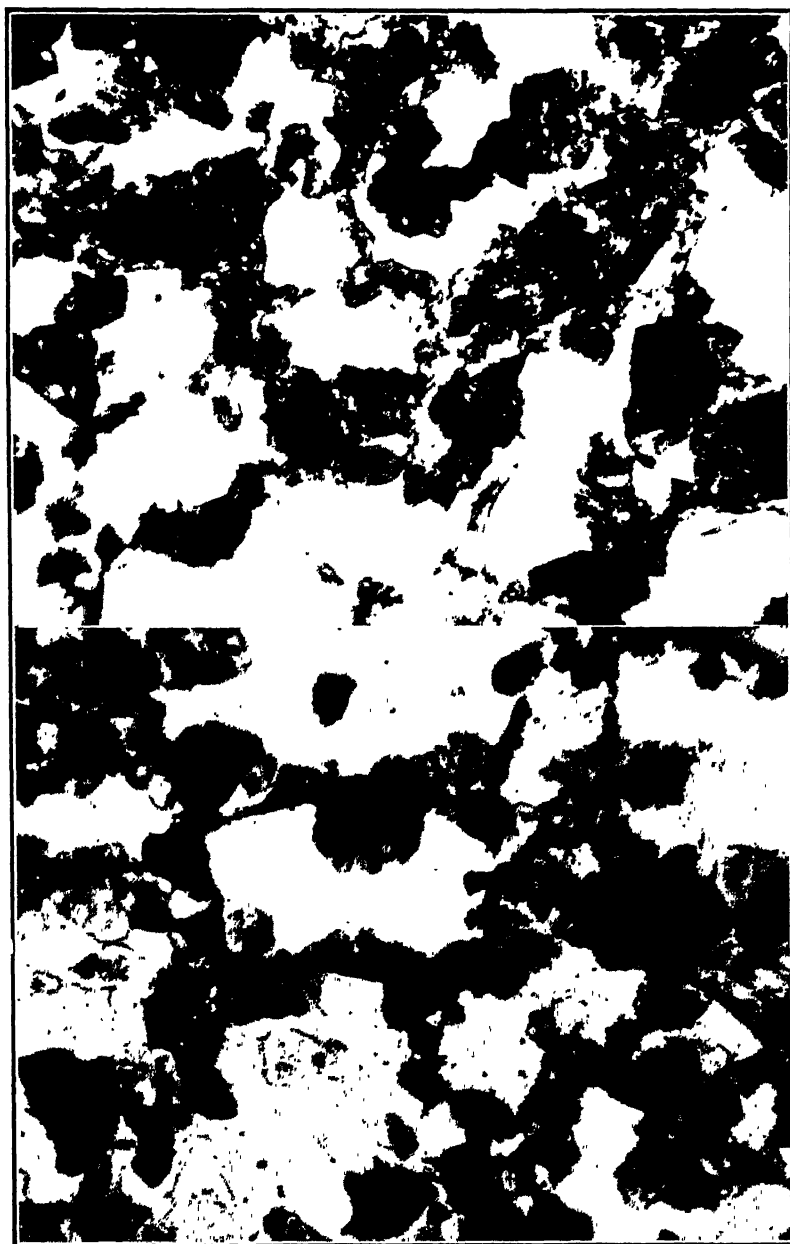


FIG. 1.—RELATIVE TIME FOR AUSTENITE (BLACK) TRANSFORMATION TO FERRITE AND CARBIDE OR MARTENSITE (WHITE) AT VARIOUS TEMPERATURES.

alloy additions we may turn to the manganese steels, since manganese is one of the very serviceable alloys for developing oil-hardening or deep-hardening qualities.

At 525° C. (975° F.) for example it is found that steels containing about 0.55 per cent carbon and a normal 0.50 per cent manganese are able to transform completely in less than 3 sec., the product being a nodular form of pearlite so fine that only rarely can lamellae be observed in the microscope at the limit of resolution. Fig. 2 shows the microstructure at 700 dia. of the product of this reaction not yet completed in a steel of about 0.55 per cent C and 1 per cent Mn after 2 sec. Some free ferrite has separated; this is the first constituent to appear and may properly be called proeutectoid ferrite. We shall have more to say of the subcritical rejection of proeutectoid constituents later. A steel of similar carbon content, but carrying 6.4 per cent Mn, transforms by a very similar mechanism, and when about 30 per cent completed, shows the microstructure of Fig. 3. Dr. F. F. Lucas, who has set new standards of photomicrography, has succeeded in resolving occasional lamellae of carbide in steels which must have undergone transformation at about this same temperature although quenched to room temperature. By no means dissimilar is the result of the same partial decomposition in the case of a steel containing 13.4 per cent Mn and similar carbon, wherein the transformation temperature was also 525° C. (975° F.) as shown in Fig. 4. In Figs. 5, 6 and 7 these structures in the same identical specimens are presented at a magnification of 3600 dia. Fig. 5 shows the imperfectly resolved product of transformation in the 1 per cent Mn steel, at 525° C (975° F.), the background being *now* martensite, of course, produced, not at 525° C. (975° F.) but during the subsequent quenching to preserve quantitatively the proportions of changed and unchanged steel. About 2 sec. were required to induce this proportion of the austenite to transform. Fig. 6 shows a similar degree of transformation to a very similar product, but here 6 per cent Mn contrived to retard the reaction sufficiently to necessitate about 2 hr. for this amount of transformation. An addition of 5 per cent Mn thus retarded the reaction roughly 3600 times. A slightly greater tendency toward the revelation of lamellae may be noted here, although the resolution of present optical systems is inadequate for their very clear depiction. In Fig. 7 it may be seen that the reaction, austenite to ferrite and carbide at 525° C. (975° F.), has proceeded again to about the same extent, but in this case the manganese content was 13.4 per cent and the time required was about 12 days. A further 7 per cent increase in manganese content reduced the rate of transformation by a factor of about 150. The carbide and ferrite contrived to distribute themselves in well formed lamellae easily resolved with the oil immersion objectives of 1.4 NA. Presumably the slower reaction rate contrives to provide diffusion facilities for the carbon and



- 2.—PRODUCT OF PARTIAL AUSTENITE TRANSFORMATION AT 525° C. (975° F.) IN A 0.55 C AND 1.0 MN STEEL. $\times 700$.
- 3.—PRODUCT OF PARTIAL AUSTENITE TRANSFORMATION AT 525° C. (975° F.) IN A 0.60 C, 6.5 MN STEEL. $\times 1200$.

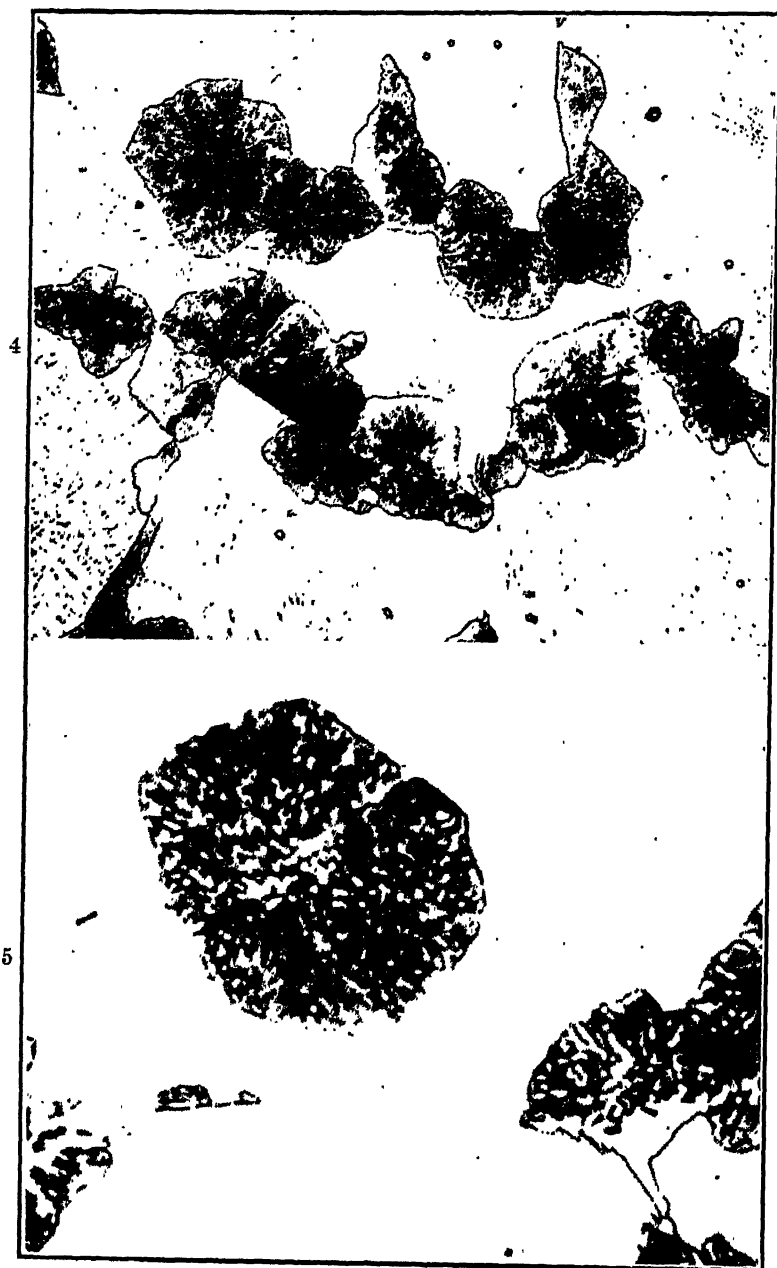


FIG. 4.—THE PRODUCT OF PARTIAL AUSTENITE TRANSFORMATION AT 525° C. (975° F.)
IN A 0.54 C, 13.4 MN STEEL. $\times 600$.
FIG. 5.—SAME AS FIG. 2. $\times 3600$.



6



7

FIG. 6.—SAME AS FIG. 3. $\times 3600$.
FIG. 7.—SAME AS FIG. 4. $\times 3600$.

as a result, the pearlite is not very unlike that formed in about 1 min. at higher temperatures in plain carbon steels. The chief difference is that increasing alloy content causes a trend from parallel plates toward the radial distribution.

Here then is the same reaction occurring at the same temperature and proceeding to one-fourth completion in a series of steels¹ of approximately constant carbon content but with manganese varying from 0.5 to 13 per cent, and requiring therefore from 1 sec. to about 1,000,000 sec. to accomplish the same destruction of austenite. It appears that



FIG. 8.—PEARLITE IN NORMAL HYPEREUTECTOID CARBON STEEL. $\times 4000$.

the first additions of manganese retard the reaction about 10 times for each per cent, but further additions above 5 or 6 per cent require increments of about 3 per cent Mn to decrease the reaction rate by the same factor. Perhaps a graphic chart of austenite proportion plotted against time may better show the nature of this reaction.

Fig. 9, illustrative of a form of chart which will be again employed, shows the proportion of austenite remaining after the lapse of any time interval from 1 sec. up to several weeks at 525° C. (975° F.), for a series of manganese steels. To show simultaneously a phenomenon requiring seconds and other phenomena occurring over periods of days requires the use of a logarithmic scale for time. All of the curves originate at the lowest ordinate or 100 per cent austenite—zero ferrite or carbide. The

¹ These steels were secured through the courtesy of Mr. Charles L. Kinney, Jr. from the Physical Laboratory, Illinois Steel Co.

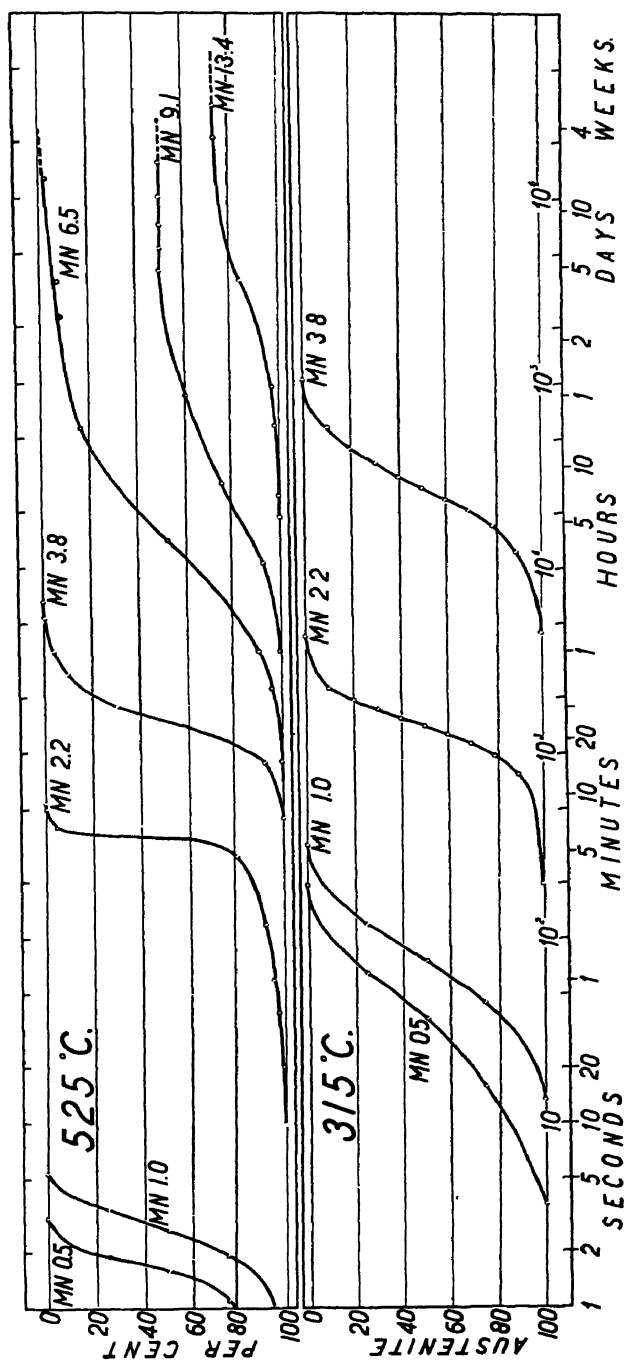


FIG. 9.—DIMINISHING PROPORTION OF AUSTENITE IN A SERIES OF MANGANESE STEELS OF ABOUT 0.55 PER CENT C AS MAINTAINED FOR TRANSFORMATION AT CONSTANT TEMPERATURE (525° C. AND 315° C.; 975° F. AND 600° F.). NOTE DISPARITY IN TRANSFORMATION RATE.

graph shows how the austenite decomposes as time passes and ultimately, when the reaction is complete, the curve reaches the topmost ordinate, zero austenite and 100 per cent ferrite and carbide. It will be observed that the steel containing 6.5 per cent Mn just reaches complete transformation, and that the steels containing more manganese (9.1 per cent and 13.4 per cent) reach a persistent condition involving no further change after many days at 525° C. (975° F.). This is merely a reflection of the circumstance that this temperature is actually above the lowest critical temperature for the manganese-rich alloys and consequently they are at equilibrium when the indicated proportions of austenite, ferrite and carbide are simultaneously present. The manganese steel containing about 6.5 per cent Mn is really not far from eutectoid, but nevertheless it too possesses a definite temperature zone of three-phase equilibrium.

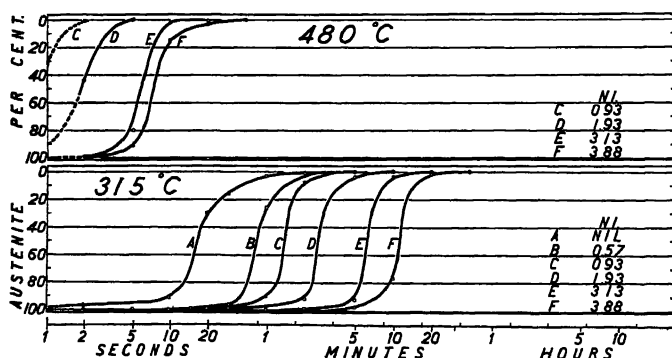


FIG. 10.—DIMINISHING PROPORTION OF AUSTENITE IN A SERIES OF NICKEL STEELS OF ABOUT 0.55 PER CENT C AS MAINTAINED FOR TRANSFORMATION AT CONSTANT TEMPERATURE (480° C. AND 315° C.; 900° F. AND 600° F.).

In the same chart, Fig. 9, are seen the transformation curves for these same steels at 315° C. (600° F.), a temperature at which any steels of more than medium carbon content transform most deliberately. At this temperature the manganese acts again as a strong retarding agent upon the reaction, the rate decreasing very roughly tenfold for each added 1 per cent Mn. As might be expected on this basis, the steel containing 6.5 per cent Mn failed to exhibit any change whatsoever from pure austenite in over a month, although it transformed, as may be seen in the chart directly above, almost completely in a week at 525° C. (975° F.).

The Nickel Effect.—Although not usually employed as an alloying agent to secure deep hardening, nickel, like almost any metal that may be added to steel, exerts a definite influence upon the rate of the reaction wherein austenite changes to ferrite and carbide. Fig. 10 presents a series of constant-temperature transformation charts, at 480° C. (900° F.) and at 315° C. (600° F.) similar to those just discussed in connection with

the effect of manganese, in which a series of steels,² with increasing nickel content are depicted: A, 0 per cent; B, 0.5 per cent; C, 1 per cent; D, 2 per cent; E, 3 per cent; F, 4 per cent. The speed of reaction becomes slower at all stages with successive nickel additions. In a broad way, at the higher temperatures, each 1 per cent addition of nickel may be said roughly to double the transformation time. At lower temperatures of transformation nickel has comparatively less effect, and this is in general the trend of all alloy additions up to a quantity whereby the critical temperatures are so far lowered as to distort completely the typical S-curves exemplified in Fig. 1 and to develop dominantly austenitic steels.

The actual critical temperatures as determined by equilibrium studies for the 0.55 per cent C-Ni steels and the 0.55 per cent C-Mn steels are not greatly unlike, as shown in Fig. 11. For this reason, it is particularly interesting to compare rates of reactions in the two series, for the complicating influences of different relations of transformation temperature

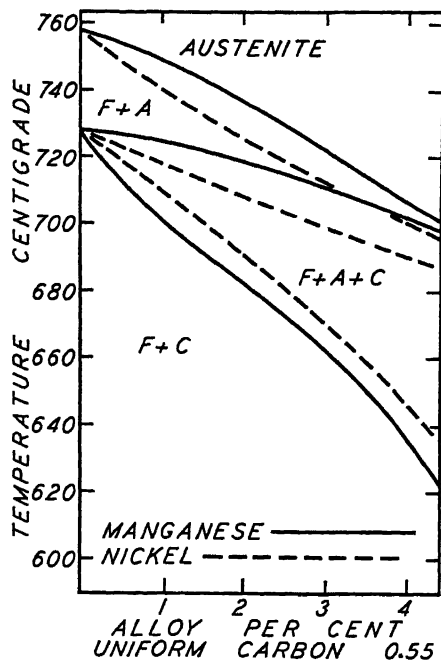


FIG. 11.—APPROXIMATE CRITICAL POINTS IN MANGANESE AND NICKEL STEELS OF ABOUT 0.55 PER CENT C AND VARIOUS ALLOY CONTENT. NOTE GENERAL SIMILARITY.

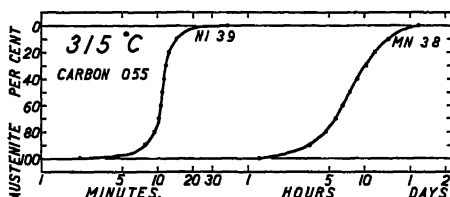


FIG. 12.—DIRECT COMPARISON OF REACTION TIME IN A NICKEL AND A MANGANESE STEEL EACH WITH ABOUT 0.55 PER CENT C AND 3.8 PER CENT ALLOY.

to critical temperatures is avoided. It will be borne in mind that all rates thus far discussed refer to steels all carrying about 0.55 per cent C irrespective of alloying element. Fig. 12 shows the compara-

² These steels were secured through the courtesy of Mr. H. J. French from the Research Laboratory, International Nickel Company.

tive rates of reaction for the similar nickel and manganese steels each with about 0.55 per cent C and about 3.8 per cent alloying element. The greater retarding power of the manganese is quite marked, for the two curves are widely separated. The particular retarding power of this proportion of manganese is roughly 50 times that of the same nickel addition.

RATE CHARACTERISTICS OF AUSTENITE TRANSFORMATION

In the reactions so far discussed we have concerned ourselves almost wholly with the transformations wherein austenite, a single phase, rejects simultaneously ferrite and carbide. It has been proposed by Hoyt that an inspection of the rate characteristics of this reaction might be illuminating and in a limited way this has been done. As a result of this mode of interpretation it appears that it is characteristic of this reaction that it proceeds, once well under way, nearly in accord with the provisions of what is known to the physical chemist as a typical first order reaction. By a "first order reaction" is designated one whose instantaneous rate at any moment is directly proportional to the amount of unchanged phase. When concurrent action of a number of atoms or molecules is demanded, the reaction follows other exponential relations; "second" and "third" order, etc. This classification of reactions is only an expression of the laws of probability—the less material to react, the less material which will react in any short interval of time.

It is however equally characteristic of our austenite reaction that it departs from the ways of perfect first order reactions in three distinct respects:

1. The reaction does not, so far as has been detected, begin at all for a very considerable time relative to the total time involved. (This period of induction, or period of nucleus formation, is greater with higher alloy content.)

2. The reaction does not even then start at maximum velocity and does not achieve maximum velocity until in general some 25 to 30 per cent of the austenite has transformed.

3. The reaction does complete itself in finite time and the very last fragments of austenite transform therefore rather faster than would be expected, though, I hasten to add, slowly enough.

In respect to the last two considerations it is only in degree that they differ from more familiar reactions of the first order in the liquid and this has probably to do with certain circumstances inherent in the solid state. As for the first departure from ideal first order reaction behavior, it must be said that this reaction displays an almost human trait, in that it just does not get started off on its task on time but once started it feels less reluctant and makes an excellent appearance of maintaining schedule. In the interest of observing that for the most part the reaction proceeds

as a first order reaction, we have but to forge the starting date and all is well, as will be seen.

For purposes of comparison, one steel with another, it has been necessary, in the preceding charts, to employ the logarithmic scale, for the

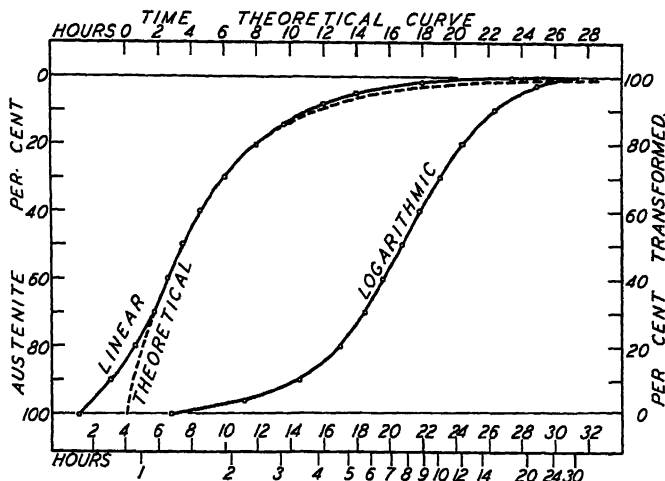


FIG. 13.—TRANSFORMATION OF AUSTENITE IN A 3.8 PER CENT MN, 0.55 PER CENT C STEEL PLOTTED ON A LINEAR AND A LOGARITHMIC TIME SCALE FOR COMPARISON WITH THE THEORETICAL FIRST ORDER REACTION CURVE.

difference in rates is too great to depict on a linear scale of time. This is somewhat confusing and I am therefore at the necessity of asking you, on the basis of a single comparison, to accept the statement that the general shape of the transformation curves shown thus far is a strong indication of the fact that they resemble first order reactions. In Fig. 13 is shown the disappearance of austenite and the formation of ferrite and pearlite for one of the steels discussed, plotted both on the logarithmic scale and on the usual linear scale. Along with the linear plot is the theoretical curve for a first order reaction of similar constants. The zero time is shifted, and the really small discrepancy is clearly indicated.

For those interested in this mathematical treatment the equation of the curve of $\log \frac{1}{1-x} = Kt$ in which x is the fractional pearlite, formed after any time interval t . This is derived from the governing circumstance in the reaction that the reacting rate is always proportional to the amount of unchanged austenite, expressed thus $\frac{dx}{dt} = K(1-x)$.

For the curve shown in the previous figure which referred to a 3.8 per cent Mn steel transforming at 315° C. (600° F.) the constant K is 0.2 (time in hours) and the reaction proceeded in its later stages precisely as though it began 4 hr. after the actual quenching to 315° C (600° F.)

and over 2 hr. after the first pearlite was produced. Seemingly the early part of the 4-hr. lag is consumed in sheer procrastination, and the latter part in activity which might at best be styled as half-hearted.

These characteristics are observed similarly for many steels and might form the basis of a profitable study into the nature of reactions in the solid.

SUCCESSIVE REACTIONS

Thus far we have considered the reaction, austenite to ferrite and carbide. But there are departures from this simple case which merit our attention as modifying our simple picture, of which two may be mentioned:

1. The case of distinctly hypoeutectoid steels rejecting only ferrite at somewhat higher temperature until the carbon concentration in the remaining unchanged austenite is increased to a point permitting simultaneous carbide and ferrite formation; and,
2. The case of steels wherein it is possible to find graphite, not carbide, as the ultimate product of austenite decomposition.

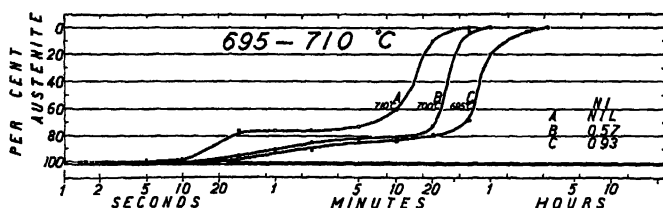


FIG. 14.—TRANSFORMATION OF AUSTENITE IN CHARACTERISTICALLY HYPOEUTECTOID STEELS AT TEMPERATURES JUST BELOW A_1 .

Both of these cases are well illustrated in the series of nickel steels with 0.55 per cent C already discussed. The steels A, B and C, with respectively no nickel, 0.5 per cent and 1 per cent approximately, all reject proeutectoid ferrite well below the lower critical temperature, as do most low-alloy steels somewhat remote from the eutectoid composition. This same reaction to form ferrite also occurs just above A_1 but, curiously enough, at a still slower rate. Subcritical decomposition of the austenite therefore proceeds in two stages: (1) austenite to ferrite and (2) austenite to ferrite and carbide. In Fig. 14 is shown the familiar plot of decreasing austenite and the two stages of the reaction are quite clearly marked out. The second stage apparently begins when the rate of reaction in the first has declined to that at which both carbide and ferrite form at equivalent rates. Separating the two stages as distinct reactions for the plain carbon steel, we find that the ferrite reaction proceeds to a point at which the austenite is reduced to three-quarters of the whole, and that, assuming a first order reaction, the constant K is 0.0183 (time in seconds) with a

time lag of 10 sec. The second stage of the transformation also approximates a first order reaction with a constant K equal to 0.003 with a time lag of 465 sec. for this reaction alone.

Three-stage Transformation.—The second case mentioned wherein the reaction is complicated by the formation of graphite is well illustrated in the behavior of 3.0 to 4.0 per cent Ni steels. These steels contrast sharply with those containing such carbide-forming elements as manganese or chromium, in which the final persistent form of carbon appears to be the carbide phase. Even in pure iron-carbon alloys there seems to be at least some reason to believe that graphite, not carbide, is the really final form, at least in ranges of composition and temperature wherein substantial atomic migration is possible. At any rate, it is rather well marked in these nickel steels that while either carbide or graphite may form, graphite is the stable phase. The fact that tons of nickel steels may contain not a milligram of graphite is dependent apparently upon the relative rates of the two reactions.

These changes may be studied easily by quenching small pieces of the steel from a temperature, for example 800° C. (1470° F.), at which a purely austenitic condition results, into a suitable bath at a temperature of about 635° C. (1175° F.) at which both the carbide and the graphite reactions proceed at measurable rates. As the decomposition of the austenite proceeds specimens may be withdrawn, quickly quenched into water, and examined microscopically. The reactions involved may be studied as closely as desired. After the austenitic steel is quenched to this temperature, small particles of ferrite are rejected within 10 sec. and may be discerned in the quenched specimen as quite distinct from the martensite background. The further rejection of proeutectoid ferrite continues for about 75 min. until it constitutes perhaps one-sixth of the volume of the steel; Fig. 15 shows the progress of the ferrite rejection. This reaction so far is almost identical with the reaction taking place in plain carbon, hypoeutectoid steels at temperatures above the lower critical, or A_1 point. But at about this stage the reaction is proceeding very slowly and just as slowly begins the simultaneous rejection of both ferrite and carbide; not, however, as lamellar pearlite. In Fig. 16 the carbide is shown darkened by sodium picrate for clarity. The proeutectoid and eutectoid ferrite are indistinguishable, and the carbide is interstitial. This reaction (austenite to ferrite plus carbide) continues until only one-quarter of the austenite remains, as in Fig. 17, and the last decomposition is at an extremely slow rate. In the photomicrograph the unchanged austenite is revealed as martensite etched to a light gray texture. After 8 hr., long before the last austenite has disappeared, graphite makes its appearance as in Fig. 18. The steel then contains four phases, austenite, ferrite, carbide and graphite. Since four phases, in three-component systems, provided only one degree



FIG. 15.—PROEUTECTOID REJECTION OF FERRITE IN A 3.9 PER CENT NI, 0.55 PER CENT C STEEL AT 635°C . (1175°F). $\times 2400$.

FIG. 16.—PRODUCTS OF AUSTENITE TRANSFORMATION IN A 3.9 PER CENT NI, 0.55 PER CENT C STEEL AFTER 120 MIN. AT 635°C . (1175°F). AUSTENITE (NOW MARTENSITE) FERRITE AND CARBIDE (BLACK). $\times 2400$.

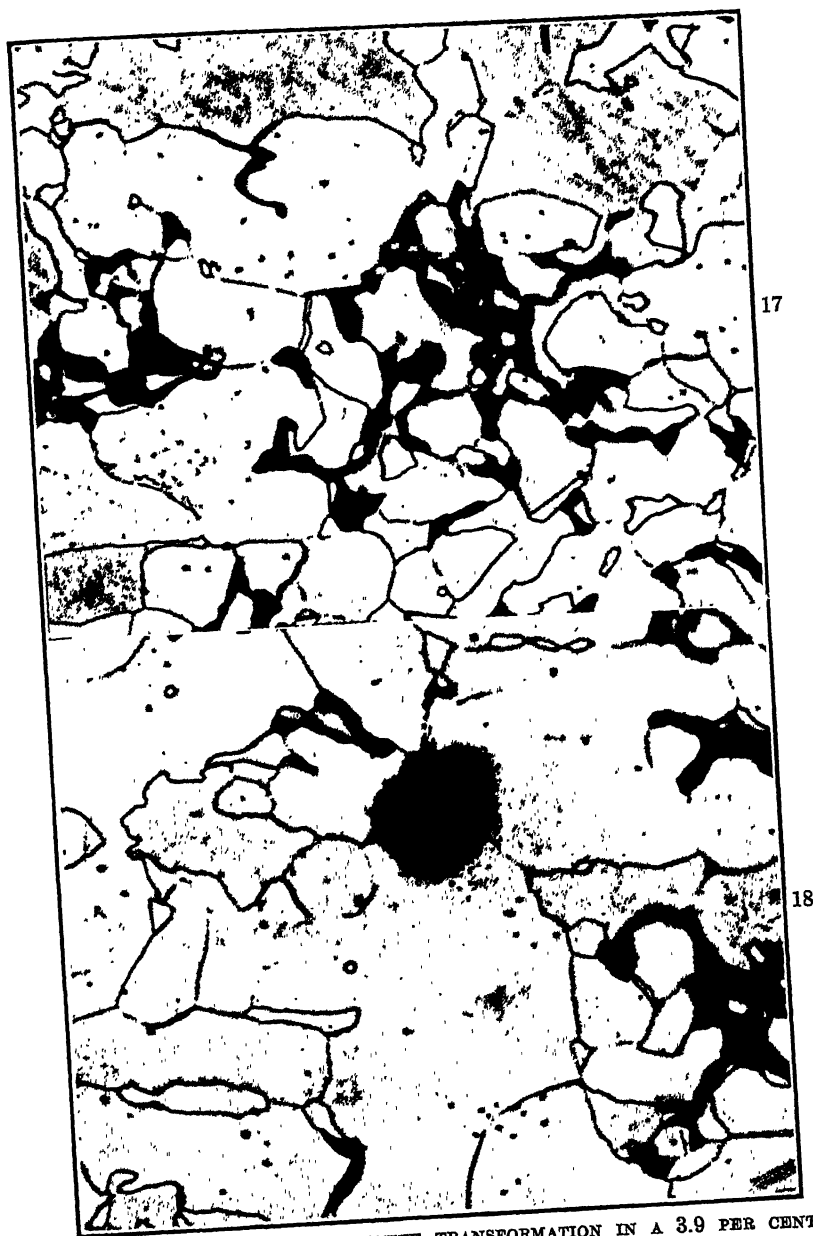


FIG. 17.—PRODUCTS OF AUSTENITE TRANSFORMATION IN A 3.9 PER CENT NI, 0.55 PER CENT C STEEL AT 635°C . (1175°F .) AFTER 240 MIN. WHEN CARBIDE PROPORTION IS AT A MAXIMUM. $\times 2400$.

FIG. 18.—FIRST APPEARANCE OF GRAPHITE (BLACK SPOT IN CENTER) IN A 3.9 PER CENT NI, 0.55 PER CENT C STEEL TRANSFORMING AT 635°C . (1175°F .) AFTER 16 HR. AUSTENITE (MARTENSITE) FERRITE AND CARBIDE (BLACKENED) AND GRAPHITE. $\times 2400$.

of freedom, monovariance, it seemed to us probable that one or more of the phases must probably disappear shortly, and in this we were not disappointed.

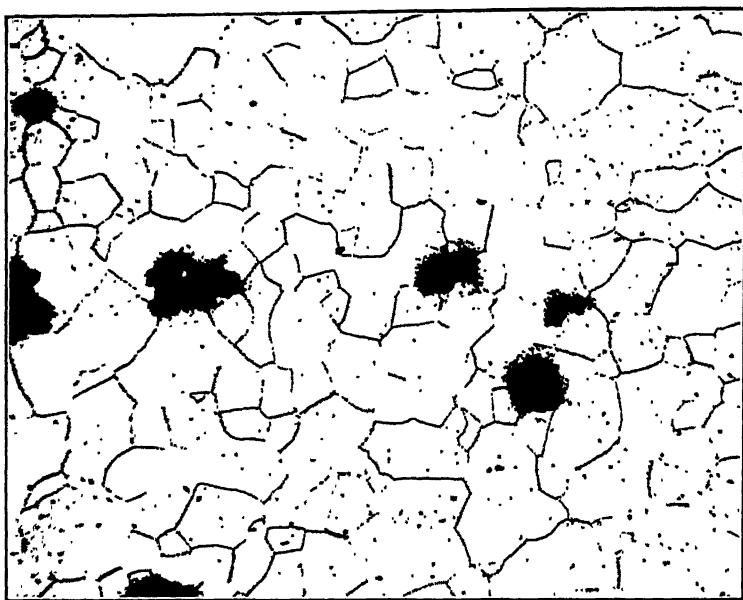


FIG. 19.—FINAL CONSTITUTION OF A 3.9 PER CENT NI, 0.55 PER CENT C STEEL TRANSFORMED FROM AUSTENITE AT 635° C. (1175° F.) AFTER 125 HR.; FERRITE AND GRAPHITE. $\times 600$.

First the austenite diminishes and disappears and almost simultaneously the carbide is used up, and finally, after about 125 hr., only ferrite

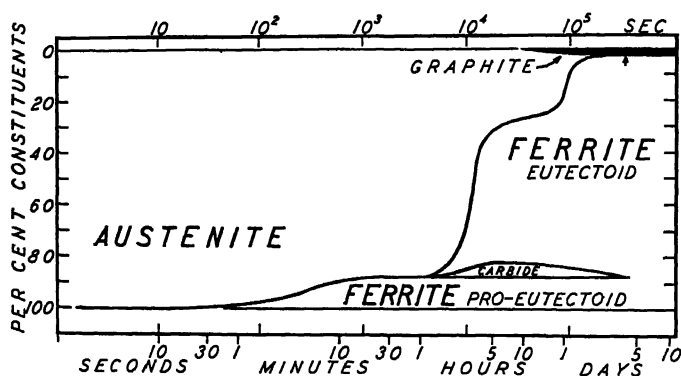


FIG. 20.—DIMINISHING PROPORTION OF AUSTENITE AND ITS PRODUCTS OF TRANSFORMATION AT 635° C. (1175° F.) IN A 3.9 PER CENT NI, 0.55 C STEEL. TIME ON LOGARITHMIC SCALE. NOTE RISE AND DECLINE IN PROPORTION OF CARBIDE.

and graphite remain, as illustrated in Fig. 19. The rate of simultaneous ferrite and carbide formation declines to a low value when only a small

amount of austenite remains and the formation of graphite and ferrite appears to begin at this low rate, augmented perhaps by the formation of the same constituents from the carbide.

The sequence of events in this 125-hr. story of the decline of austenite is shown in the time chart of Fig. 20. This curve, again, is plotted on a logarithmic time scale and the ordinate is used to plot the proportion of the various constituents on the basis of the entire steel being 100 per cent. The austenite, freed of its supersaturation in ferrite, begins to transform in the manner of the other steels shown, after the lapse of $1\frac{1}{4}$ hr. The proportion of carbide reaches a maximum, then declines and finally disappears, at which point no distinction is made between the ferrite of proeutectoid and that of eutectoid origin; nor is there any distinction evident in the microstructure. The rate of graphite formation is much lower than that of the earlier carbide separation, which, of course, is only a necessary condition for the existence of any carbide at all. This reaction well illustrates that the less stable of two possible products of reaction may form at any time if its rate of formation, for any reason, is much higher than that of the more stable phase. Actually the temperature here selected is relatively more favorable for the graphite reaction rate than temperatures even a little lower, for graphite, although undoubtedly still the stable form, failed to appear in a period of weeks.

We have observed that this same steel apparently arrives at a persistent state at higher temperatures, above the lower critical point wherein the three phases—ferrite, austenite and graphite—are content to exist peacefully together forever. But, curiously enough, the rates of reaction are even slower than at the temperature just considered. This would correspond to the temperature zone of three phases in the chromium or manganese steels wherein austenite, ferrite and carbide are at equilibrium. However, by the time this state is reached, one is very likely to decide that the span of human life is not sufficiently long to admit of curiosity on this point, and, perhaps to feel that, so far as any emotion on our part is concerned, austenite may transform to graphite or not as it pleases.

THREE-PHASE EQUILIBRIUM

As a test for the correctness of the view that three phases are really in equilibrium at certain temperatures in alloy steels of the carbide-forming type, it seemed advisable to produce if possible the same constituency by two different reactions at the same temperature in the same steel. To make doubly certain on this point it would be preferable to first examine the two starting materials microscopically. Fig. 21 shows the microstructure of a 1.20 per cent C, 6.2 per cent Mn steel quenched to room temperature in the wholly austenitic, though unstable condition. In the temperature range of about 665° C. (1230° F.) this steel, it is

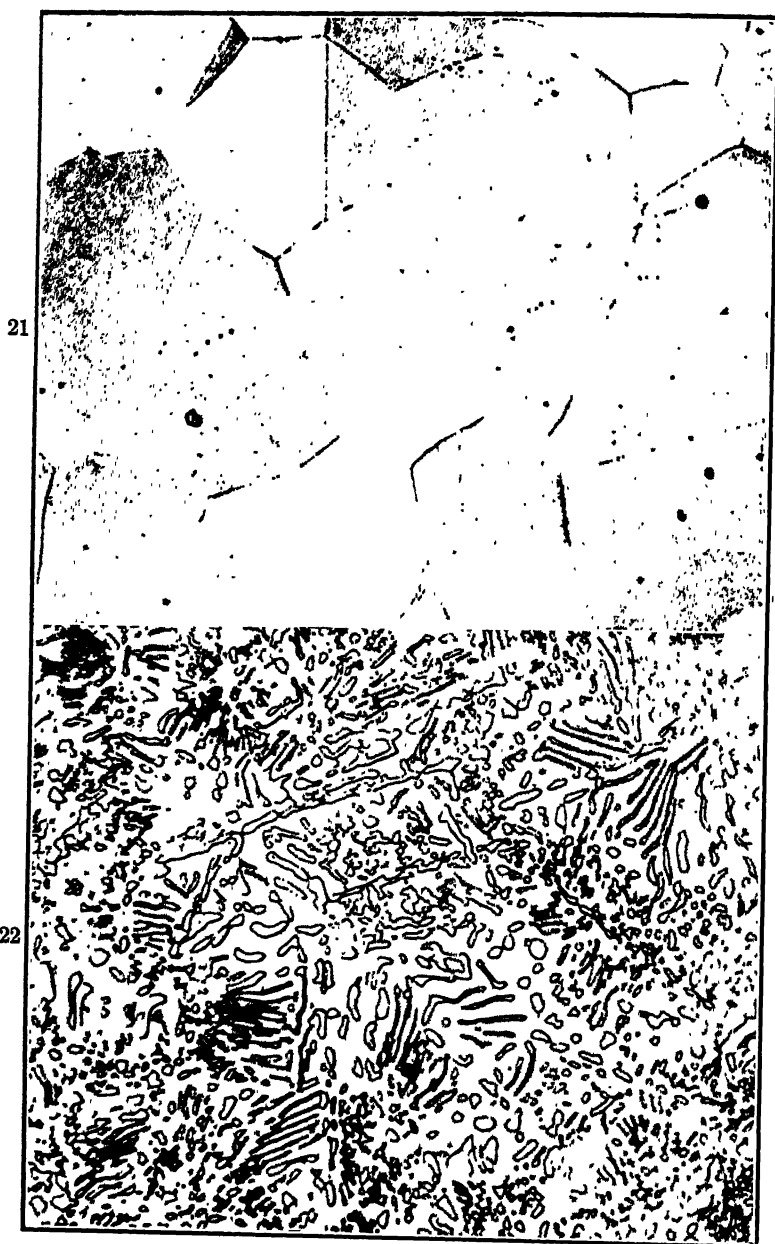


FIG. 21.—PURELY AUSTENITIC STRUCTURE IN A 6.2 PER CENT MN, 1.20 PER CENT C STEEL AFTER QUENCHING FROM 1100°C . (2010°F .), PERSISTENT AT ROOM TEMPERATURE. $\times 600$.

FIG. 22.—PEARLITIC STRUCTURE IN STEEL OF FIG. 21 (6.2 PER CENT MN, 1.20 PER CENT C) AFTER 100 HR. AT 600°C . (1110°F .). $\times 2400$.

believed, should exist at equilibrium as a mixture of ferrite, carbide and austenite. It can, however, by suitable long time heating at a lower temperature, *e. g.*, 600° C. (1110° F.), be rendered wholly pearlitic—ferrite and carbide. Thus in Fig. 22 it will be seen that this same steel is composed wholly of ferrite and carbide. If samples of this steel in each of the two conditions are introduced into a constant-temperature bath at 665° C. (1230° F.) they should, if our premises are correct, set about making such changes as will bring them to the same state, although, we may be sure, at their own convenience. As a matter of fact, this is correct, although I will confess that I was shown to be properly a "prophet without honor in his own land," for the two conditions approach equilibrium at relative rates quite the reverse from my prediction. The austenitic steel immediately begins to reject proeutectoid carbide even after a few seconds, and after 3 min. exhibits the structure of Fig. 23. The carbide rejection in very perfect plates is a proeutectoid reaction analogous to that in the hypoeutectoid nickel steels, but proceeds a little less rapidly. When some considerable carbide, perhaps 10 to 12 per cent of the volume of the steel, is formed, nodular pearlite begins to form (Fig. 24). This reaction continues until only about 35 per cent of the original austenite remains after nearly 200 hr. and thereafter the proportion is constant; Fig. 25 shows how the carbide as plates and that of the pearlite has coalesced.

In the meantime, after about 40 hr., some austenite has formed in the pearlitic specimen in sufficiently large masses to be recognizable in the microscope, for after quenching they remain unchanged. Fig. 26 shows the early stages of austenite formation in the pearlitic specimen. Due presumably to the very considerable migration of both carbon and manganese required in the formation of austenite by interaction of ferrite and carbide, the process is extremely slow, and only after 300 or 400 hr. is any considerable amount of austenite properly divorced, as in Fig. 27. Austenite etches somewhat darker than ferrite. After about 500 hr. the steel in the two original conditions has arrived at equilibrium and each specimen contains about 35 per cent austenite. The similarity of the end products from the two conditions is illustrated in Figs. 28 and 29, which have been etched in carbide-blackening sodium picrate solution. The austenite fields may be recognized by their freedom from carbide particles. The coarser particles mark the specimen which began as austenite. A reference to Fig. 30 will show how the two reactions reach the same equilibrium after sufficient time intervals. If at equilibrium three phases were not present simultaneously, it would have been impossible to produce the absent phase or phases in both specimens to make up the final constituency of austenite 35 per cent, carbide 18 per cent and ferrite 47 per cent.

23



24



FIG. 23.—FIRST STAGE OF AUSTENITIC TRANSFORMATION IN A 6.2 PER CENT MN, 1.20 PER CENT C STEEL AT 665° C. (1230° F.) AFTER 3 MIN. NOTE CARBIDE PLATES. $\times 2400$.

FIG. 24.—AUSTENITE TRANSFORMATION TO NODULAR PEARLITE IN STEEL OF FIG. 21 (6.2 PER CENT MN, 1.20 PER CENT C) AT 665° C. (1230° F.) AFTER ABOUT 30 MIN. $\times 2400$.



FIG. 25.—ORIGINALLY AUSTENITIC STEEL OF FIG. 21 (6.2 PER CENT MN, 1.20 PER CENT C) AT EQUILIBRIUM AT 665° C. (1230° F.) AFTER ABOUT 480 HR. AUSTENITE, CARBIDE AND FERRITE. $\times 2400$.

FIG. 26.—FIRST FORMATION OF AUSTENITE IN PEARLITIC STEEL OF FIG. 22 (6.2 PER CENT MN, 1.20 PER CENT C) AFTER ABOUT 40 HR. $\times 2400$.



FIG. 27.—ORIGINALLY PEARLITIC STEEL OF FIG. 22 (6.2 PER CENT MN, 1.20 PER CENT C) APPROACHING EQUILIBRIUM AT 665° C. (1230° F.) AFTER ABOUT 480 HR. NOTE COALESCENCE. $\times 2400$.

FIG. 28.—EQUILIBRIUM AT 665° C. (1230° F.) IN ORIGINALLY AUSTENITIC STEEL OF FIG. 21. SODIUM PICRATE AND NITAL ETCH. $\times 2400$.

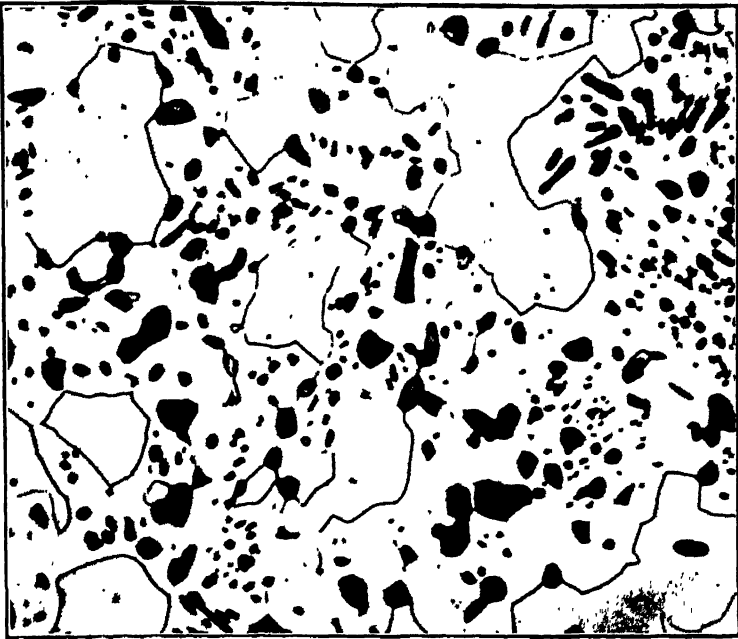


FIG. 29.—EQUILIBRIUM AT 665° C. (1230° F.) IN ORIGINALLY PEARLITIC STEEL OF FIG. 22. SODIUM PICRATE AND NITAL ETCH. $\times 2400$.

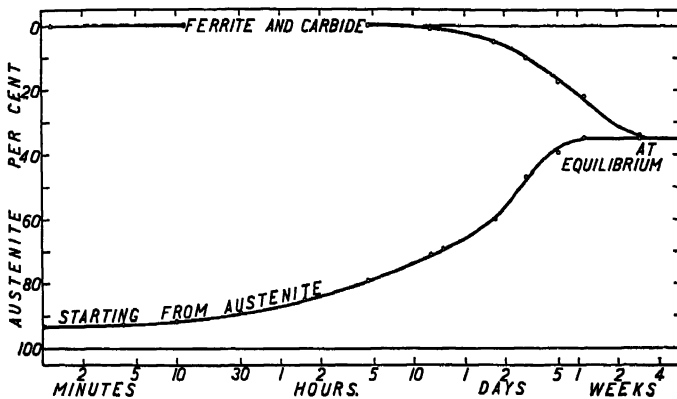


FIG. 30.—TRANSFORMATION IN A 6.2 PER CENT MN, 1.20 PER CENT C STEEL AT 665° C. (1230° F.) TO BRING ABOUT EQUILIBRIUM FROM TWO UNSTABLE CONDITIONS. TIME ON LOGARITHMIC SCALE.

IS MARTENSITE AN INTERMEDIATE STAGE?

It is by no means an innovation in Howe Memorial Lectures to introduce a word referring to the behavior of martensite. There are good reasons to suspect that martensite might be the universal first product of austenite decomposition—regardless of the temperature at which it occurs, and that pearlite and troostite are then secondary products of the reaction. I must admit that while I have not inclined to that view, it has seemed a very difficult task to assemble any complete proof which would vindicate my opinion to the contrary. The evidence which Mr. Davenport has secured from the arrested transformations has been, in the main, of a nature to substantiate the view that martensite forms only at low temperature and is not an intermediate between austenite and pearlite, and yet in the last analysis perhaps some may regard this evidence as not quite decisive. It has occurred to us, in view of these rate studies, that a simple test can be made of that point. If the rate of martensite destruction is higher than the rate of austenite decomposition, then by no mechanism can it form even as an intermediate. Fortunately in some of the manganese steels this test can be made easily. In a single specimen austenite and pure martensite of the same composition can be produced by refrigerating the specimen to liquid-air temperatures after quenching to preserve austenite. The martensite thus formed in a steel containing 6.48 per cent Mn and 0.92 per cent C, Fig. 31, is seemingly an example of often described, but difficultly realized, "freshly quenched martensite," for it remains entirely white even after prolonged etching, and reveals very little detail of any sort. But this martensite is not very unlike any other in that it is persistent only at room temperature or below, and ready to relieve its tremendous supersaturation upon the first substantial rise in temperature. If, then, the temperature is abruptly raised to say 525° C. (975° F.) it is possible to observe both austenite and martensite reacting side by side at the same temperature to form ferrite and carbide. In Fig. 32 is seen the result of the transformation after the lapse of 2 min. The martensite has rejected its carbide, the particles of which have grown to microscopic dimensions, while the austenite remains wholly unchanged. Indeed, the carbide particles are already of such magnitude that they coalesce further at a very slow rate. After the lapse of 1 hr. the austenite begins to transform to ferrite and carbide by the mode characteristic of the temperature and nodules of fine pearlite are apparent, as in Fig. 33. The old martensite needles are still marked out clearly by their characteristic sorbitic appearance and in some cases have served—along with grain boundaries—as nuclei for the nodular decomposition of the austenite. After permitting the specimen to remain at 525° C. (975° F.) for 24 hr., much of the austenite is transformed to fine pearlite, but the originally martensitic regions are still clearly differentiated, as in Fig. 34. The



31



32

FIG. 31.—AUSTENITE (BACKGROUND) AND "WHITE" MARTENSITE PRODUCED BY REFRIGERATION AT -190°C . (-310°F .) IN A 6.5 PER CENT Mn, 0.92 PER CENT C STEEL. $\times 2400$.

FIG. 32.—AUSTENITE (BACKGROUND) AND COARSE SORBITE (DARK NEEDLES) PRODUCED FROM MARTENSITE (FIG. 30) AT 525°C . (975°F .) IN 2 MIN. $\times 2400$.



FIG. 33.—NODULAR PEARLITE FORMING FROM AUSTENITE IN STEEL OF FIG. 30 .
MARTENSITE IS COMPLETELY DESTROYED. $\times 2400$.

FIG. 34.—AUSTENITE LARGELY TRANSFORMED TO FINE PEARLITE IN STEEL OF F
WITH SORBITE MARKING ORIGINAL MARTENSITE NEEDLES. $\times 2400$.

disparity in rates of the formation of carbide and ferrite in the two constituents austenite and martensite at this temperature is very great; martensite breaking up thousands of times faster than the austenite can transform. Similar tests on ordinary, or aged, martensite in carbon steels indicate similar differences in rate of reaction in comparison with austenite, as shown above. One is therefore forced to the conclusion that pearlite is the direct product of austenite decomposition without any intermediate step.

REACTIONS OF RAPIDLY DIMINISHING RATES

The purpose of heating a tool steel, prior to hardening by quenching, is primarily to dissolve an adequate proportion of carbon in the austenite.

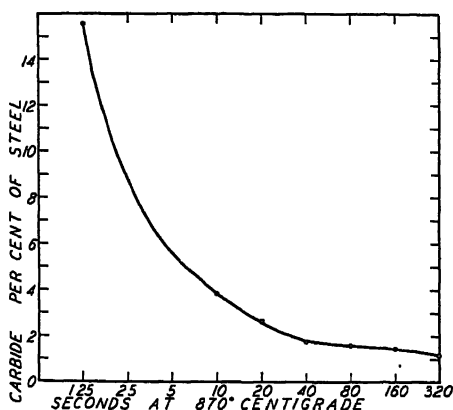


FIG. 35.—PROPORTION OF CARBIDE (AS PERCENTAGE OF TOTAL STEEL) REMAINING AFTER INDICATED TIME INTERVAL AT CONSTANT TEMPERATURE PRIOR TO QUENCH.

High-carbon steels heated to a temperature below that of the A_{cm} point will, of course, always contain residual undissolved carbide particles, but even eutectoid steels reveal residual carbide in many instances of successful hardening. The rate of the solution of carbide in the austenite, established almost at the instant the steel reaches the heating temperature, therefore has interested us, as possibly possessing unusual variations. By means of microscopic examination it may be seen that much of the carbide of carbon tool steels is dissolved after a few seconds at suitable temperature, for example 870° C. (1600° F.), but that, notwithstanding, even after heating several minutes some carbide still remains. For following more precisely the solution of carbide, actual separations of that phase in specimens maintained at the heating temperature for successively longer intervals have been made and the results are shown in Fig. 35. It should be mentioned that the accuracy improves in the specimens from the longer times at temperature due to the prevalence of larger particles; however, we feel certain the error is less than 5 per cent of the percentage

plotted in each of the cases. The determinations were made by Dr. Florence Fenwick and Miss Elizabeth Keedick, who suggested several improvements upon the usual separation methods. If one attempts to estimate the nature of this reaction it will be found that carbide is disappearing in the early stages of the reaction at a very high rate, which is about proportional to the square of the residual carbide, but after some

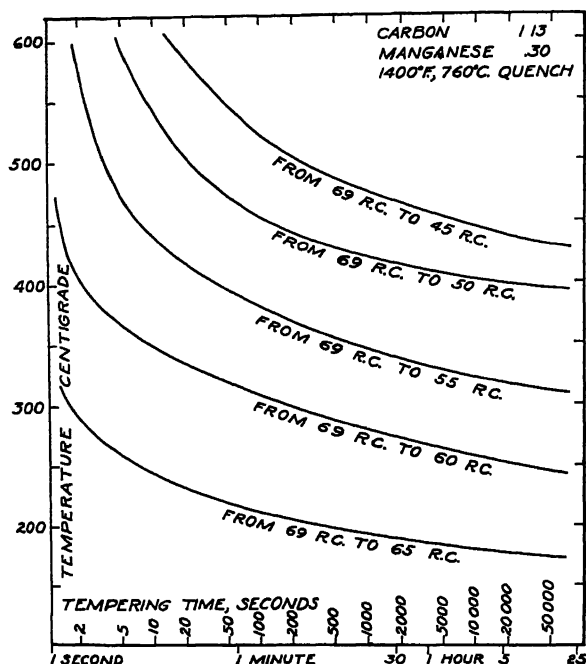


FIG. 36.—TIME-TEMPERATURE RELATIONSHIP FOR VARIOUS DEGREES OF SOFTENING OF QUENCHED STEEL BY TEMPERING.

minutes the rate is diminishing in accord with very different relations. Clearly there is no real mechanistic basis for a comparison with ordinary chemical reactions, even though statistically the same sort of analysis may be made. In point of fact, in the 1.0 per cent C steel depicted in the figure traces of carbide remain after 1200 sec. but not after 3600 sec. The small specimen employed reached substantially the temperature for the carbide solution in $1\frac{1}{4}$ sec. The shape of the curve, plotted as it is on a logarithmic scale of time, shows how the rate is decreased tremendously with the removal of the disappearing phase.

Another reaction which occurs with an originally high, but rapidly diminishing, velocity is the coalescence of carbide particles. Assuming that martensite contains only an atomic dispersion of carbon, or at most a molecular distribution of cementite, it is now generally believed that the softening of steels by tempering is a process involving mainly carbide

particle coalescence. As yet there is no correlation between actual average particle size and hardness, but assuming that a chosen hardness value corresponds to some certain average particle size, then one may measure the time and temperature combinations which will produce a definite degree of softening and accordingly an equivalent degree of carbide coalescence. It is found, as shown in Fig. 36, that the first seconds at tempering temperature are very effective in this respect, but that after a time succeeding minutes or hours accomplish very little in softening the steel. The curves represent the time-temperature requirements for several degrees of tempering. It becomes clear from these charts why it has been possible to give little attention to the time of tempering so long as it lies within practical limits; for in the case of many steels 75 per cent of the softening obtainable by tempering for 25 hr. is realized in as brief a time as 20 minutes.

Both of the carbide reactions just discussed are primarily diffusion phenomena; the one toward homogeneity and the other away from the same state. However, both have to do with a migration of carbon through successively longer paths and with successively lower concentration gradients. The path of carbon migration begins with almost atomic distances and later it unavoidably involves distances of millions of atomic layers. It is then, perhaps, not surprising that the rates vary so greatly as the process advances, and that for practical purposes a steel during tempering is often regarded as reaching a persistent condition of inactivity.

SUMMARY

1. A basis for evaluating the contribution of any alloy addition toward the development of deep-hardening or air-hardening quality in steel has been suggested, dependent upon the effect of the addition to retard transformation in the 600° to 500° C. range. This is the only fundamental property involved in securing the final quality of hardening without drastic quench. An element, manganese, contributing very greatly to this effect has been contrasted with an element, nickel, which shows only a little retarding effect upon the transformation in the significant range.

2. A series of similar steels differing substantially only in manganese content has been examined for rate of transformation, and a total range of transformation velocity covering about 1 to 1,000,000 is revealed.

3. Graphite has been found to be the stable form of carbon in 0.50 per cent C, 3.5 Ni steels free from significant amounts of other elements. Nevertheless, cementite, because of its high speed of formation, is found to form in large proportion even though it is less stable than graphite. The relative velocities of the reaction producing carbide and that producing graphite are considered to be the cause of the presence of carbide alone in nickel steels in common use.

4. A stable condition of three phases, ferrite, austenite and carbide in equilibrium is found to exist in certain manganese steels. This condition ultimately results after long heating at a proper temperature whether the original metal be austenitic or pearlitic. The state of three-phase equilibrium is reached, however, much more quickly when the starting material is austenite.

5. From the observation that "white martensite" is converted into a coarse ferrite-carbide aggregation thousands of times faster than is austenite of the same composition, it is concluded that martensite cannot be an intermediate state in the austenite-pearlite reaction.

6. Almost all of the reactions so far discussed reveal a velocity pattern very nearly that of simple first order chemical reactions. There are, however, reactions in steel which begin at very high velocity and then soon slow up to a point at which it is barely possible to find any further change whatever. Two examples of such reactions are presented; the solution of carbide in austenite at a temperature above A_{cm} , and the coalescence of carbide during tempering. In both of these reactions, carbon diffusion begins with steep concentration gradients and short paths of migration, but such paths rapidly lengthen and the gradients become less and less pronounced as the process continues.

And now that you have generously given your attention to these matters of achieving equilibrium in steel, I must confess that I have maliciously withheld the last sentence of my quotation from Dr. Howe's book lest you see only too plainly, before I began, a possible significance in it. It reads, "To all of this the busy reader may reply patly, that if that is all he may as well stop at this point in the present chapter, and if he does, I do not see that I can make any effective rejoinder, inclining to admit that if I were in his place, I too might."

Before I conclude this ninth Howe Memorial Lecture, it is my pleasant duty to acknowledge the source of the observations which I have described in all too many words. The subject matter was collected almost wholly from the various studies of my associates at the United States Steel Research Laboratories and I am particularly indebted to Mr. E. S. Davenport, Mr. W. S. N. Waring, Dr. R. H. Aborn, Mr. E. L. Roff, Mr. J. J. B. Rutherford and Mr. G. E. Guellich. To Dr. Johnston, Director of Research, United States Steel Corporation, is due my deepest gratitude for the encouragement to attempt the much-needed physical-chemical mode of attack on solid-steel problems.

As is the custom, may I suggest a moment of silence in honor of Henry Marion Howe, in whose memory we have met today.

Sinter in Blast-furnace Burdens

BY ROBERT McCLURKIN,* NORTH TONAWANDA, N. Y.

(New York Meeting, February, 1932)

OVER a long period of time considerable attention has been paid to the chemical properties of the materials entering the iron blast-furnace charge. Infinite care has been used in the selection of materials having the correct chemical composition. Little attention has been paid to the physical properties of either the ore, coke or limestone. Until comparatively recent times the coke as produced, as well as the ore, was charged into the furnace without any attempt to maintain uniformity in physical size. Recently some work has been done along the lines of sizing of coke and in some cases the sizing of ore has been applied. In each instance marked results in the efficiency of operation have been attained. The effect of changing the physical size of the materials entering the burden has been reflected directly in the coke consumption. From the experience of operators and the results of numerous investigations which have been conducted on blast-furnace materials, it may be stated definitely that the physical properties of the materials entering the charge have as much bearing on the efficiency of the process as the chemical properties of these materials.

STRUCTURE OF SINTER

On the Continent and more recently in this country iron-ore sinter has been introduced in blast-furnace burdens. The effect of the use of sinter has resulted in a material reduction in the coke consumption and an increase in the capacity of the furnace. The effect of the use of sinter is due undoubtedly to its porosity and to its physical size and, incidentally, to the chemical condition of the iron in the sinter and to the absence of combined water. Compared with Mesabi ores, all sinters are generally larger in size than the ore particles, and the structure of the sinter differs considerably from the structure of the ore. In sinter the mass is porous and open and makes available a great deal of surface for gas contact during the process of reduction. Most ores are relatively dense and nonporous and when the particle size is large the time element required for reduction is materially increased.

The result of a very thorough investigation on iron-ore sinter by Schwartz,¹ has shown that sinter is completely cellular in structure and

* Manager, Tonawanda Iron Corporation.

¹ G. M. Schwartz: Iron-ore Sinter. *Trans. A. I. M. E.* (1929) **84**, Iron and Steel Div., 39-67.

that the porosity extends throughout the mass; also, that the pores are very abundant and that they occur in large as well as small sizes. He gives the result of an examination of a sample of sinter made of Mesabi hematite ore and shows that in an area having a diameter of 0.77 mm. there existed approximately 100 cells. As indicated above, the presence of these cells very materially increases the efficiency of the gas-solid contact in the shaft of the blast furnace.

SIZE OF MATERIALS IN BLAST-FURNACE BURDEN

In order to show the difference in size of the materials which enter the blast-furnace burden, it may be of interest to mention that an index of

TABLE 1.—*Screen Analysis of Typical Samples of Flue Dust, Mesabi Ore and Sinter*

Size		Flue Dust		Mesabi Ore		Sinter ^a	
Mesh	Inches	Per Cent	Cumulative Per Cent	Per Cent	Cumulative Per Cent	Per Cent	Cumulative Per Cent
	1.0					25.54	99.28
	0.5					20.00	73.74
2	0.437			29.70	99.97		
	0.12	00	00			26.45	53.74
8	0.097	0.40	100.42	25.72	70.27	15.42	27.29
20	0.034	1.20	100.02	12.30	44.55	8.27	11.87
40	0.015	10.41	98.82	9.51	32.25	2.57	3.60
60	0.0087	21.60	89.41	7.87	22.74	0.66	1.03
80	0.0068	7.33	67.81	1.49	14.87	0.21	0.37
100	0.0055	16.40	59.48	1.34	13.38	0.16	0.16
Through 100	0.0055	43.08	43.08	12.04	12.04		
Total		100.42		99.97		99.28	

^a P. G. Harrison: Sintering Limonitic Iron Ores at Iron-ton, Minnesota. *Trans. A. I. M. E.* (1930) 90, Iron and Steel Div., 346.

each size of material may be obtained by multiplying the screen size in inches by the percentage retained between various screens. The sum of the values found gives an indication of the size of the ore sinter or material charged. In a representative Mesabi ore where approximately 30 per cent is retained on a 2-mesh screen and 25 per cent on 8-mesh, the average size of the particle in the mass is approximately 0.22 in. dia. A representative sample of flue dust gives a result which indicates an average diameter of particle of 0.009 in. In comparing these with sinter, it may be shown that in general the average size of the particle of sinter charged to the blast furnace is 0.64 in. The average diameter of the sinter particle is about three times that of ordinary Mesabi ore. The

sinter is very cellular and open while the ore particle is more or less dense and does not allow the gas to penetrate. The results that have been obtained by applying iron-ore sinters to blast-furnace burdens undoubtedly are due mainly to the physical size and structure of the sinter rather than to its chemical analysis.

Table 1 gives the screen analysis of typical samples of flue dust, Mesabi ore and sinter and these values have been plotted in a curve in Fig. 1.

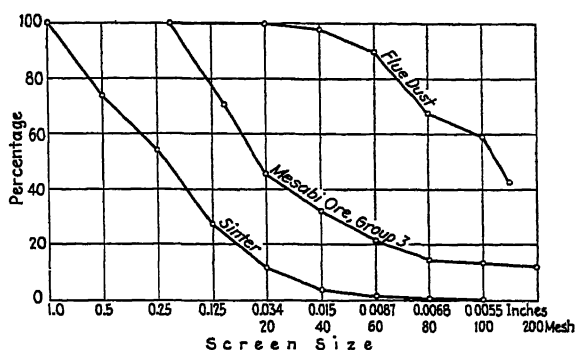


FIG. 1.—SCREEN ANALYSIS OF TYPICAL SAMPLES OF FLUE DUST, MESABI ORE AND SINTER.

CHEMICAL PROPERTIES OF SINTER

The fact must not be overlooked that sinter has some chemical properties, as well as physical, which act in the burden to increase the efficiency of the smelting process. It may be shown that the chemical properties are not as valuable as the physical; however, they are by no means a detriment. Schwartz² has shown that the presence of silica in blast-furnace sinter increases the strength of this sinter and forms an iron silicate. Incidentally, it is also shown that this iron silicate has a lower melting point than most of the constituents in the burden. The melting point of Fe_2SiO_4 is 1335°C . while the melting point of magnetite is 1538°C . and the melting point of Fe_2O_3 is 1550°C . It has also been shown by Schwartz that 90 to 99 per cent of the melting iron is combined as Fe_3O_4 or $\text{FeO}.\text{Fe}_2\text{O}_3$. A considerable portion of the iron is present as Fe_3O_4 . Metallic iron is not generally present. Because iron silicate has a lower melting point than the other constituents it follows that less heat is required in the reduction of the silicate. In sinter the silicate is more or less loosely combined with the iron and owing to the weak bonding it is quite probable that the reduction of the iron in this form is carried on with ease.

It has been shown that Fe_2O_3 requires more heat for reduction than Fe_3O_4 . It is generally stated that Fe_2O_3 requires approximately 3240

² Reference of footnote 1.

B.t.u. per pound of Fe and that the reduction of Fe_3O_4 to Fe requires 2970 B.t.u. per pound of Fe. The difference is 270 B.t.u. per pound of Fe. This difference is small but has its effect in reducing the coke requirement. It may be shown that approximately 600,000 B.t.u. would be saved per ton of iron if all of the iron originated from sinter and if the iron in the sinter were in the form of Fe_3O_4 rather than Fe_2O_3 . Assuming a ton of iron to contain approximately 93 per cent Fe, the iron reduced from Fe_3O_4 would be 2080 lb. at 2970 B.t.u. per pound or 6,177,600 B.t.u. per ton. In case of reduction from Fe_2O_3 the 2080 lb. of iron would require 3240 B.t.u. per pound or approximately 6,739,200 B.t.u. per ton, which indicates a difference in thermal requirement of some 561,600 B.t.u. per ton. The use of Fe_3O_4 in the burden would require approximately 39 lb. of carbon or 43 lb. of coke less than the requirement for Fe_2O_3 . From the above it may be concluded that the limit of fuel reduction which may be obtained through the use of magnetite in sinter will be approximately 43 lb. of coke. On the other hand, practice has shown that the use of sinter in burdens has made several hundred pounds difference in the coke requirement for the process. It may be said further therefore that the effect of the physical size and structure of the sinter has four or five times the value of chemical properties of the sinter in reducing the quantity of fuel required for the production of a ton of iron.

EFFECT OF SIZE OF MATERIALS

There has been considerable experience abroad and some practice in this country in introducing sized materials into blast-furnace burdens. In one instance a change in the physical size of the materials was introduced and the coke consumption was reduced from 2700 to 2040 lb., and a later change in the size of the materials used effected a reduction in the coke consumption from 2042 to 1700 lb. Each time a more efficient gas-solid contact was attained, as indicated by an increase in carbon dioxide in the top gases and a reduction of coke used per ton of iron. The change in the size of the physical properties of the materials used resulted in a more uniform flow of the gases up through the shaft of the furnace and also in better working of the furnace.

In the case cited above no change was made in the chemical properties of the coke, stone or ore. The physical size of the ore resulted directly in approximately 1000 lb. reduction in coke consumption. This experience may be taken as an example of a change in physical size rather than in chemical composition of materials used in the burden. It is obvious that no such reduction in coke consumption could be obtained by merely changing the chemical composition of ordinary materials entering the burden.

EFFECT OF SINTER

More recently the use of sinter has been adopted on this furnace and a further reduction in coke consumption has been effected. The operators have also noticed the ability of the furnace to take higher blast heats and to operate more smoothly and without checking. Some of the finer ores were eliminated from the burden and 30 per cent sinter was substituted. The elimination of fine ores, which have a particle size of approximately 0.2 in., and the substitution of sinter, which has a particle size of 0.6 in. and a more cellular structure, resulted in smoother operation and an increase in furnace capacity with a decrease in coke consumption.

At another plant during a period of five months in 1930 the average coke consumption was 2065 lb. per ton of pig. During the period approximately 6 per cent sinter was used in the ore mix. An increase to 16 per cent sinter in the ore mix resulted in an operation with 1955 lb. of coke per ton of iron for a period of three months.

TABLE 2.—*Operation of a Group of Furnaces during One Year*

Year, 1931	Product, Tons	Wind, Cu. Ft.	Blast Temperature, Deg. C.	Coke, Lb. per Ton	Sinter Used, Per Cent	Ore Scale, Per Cent in Sinter	Mesabi Ore Used, Per Cent	Flue Dust, Lb. per Ton
January.....	705	49,000	1,200	1,863	47	26	36	140
February.....	810	60,000	1,160	1,904	44	31	32	225
March.....	735	54,000	1,080	1,894	48	32	28	165
April.....	770	57,500	1,050	1,885	50	28	28	195
May.....	780	61,000	1,050	1,875	41	33	27	180
June.....	735	51,500	1,070	1,769	74	22	13	160
July.....	720	56,000	1,105	1,888	48	27	24	135
August.....	750	57,000	1,210	1,951	45	36	25	75
September.....	785	51,000	1,250	1,693	48	42	28	80
October.....	720	49,000	1,230	1,693	44	34	24	85
November.....	805	51,500	1,255	1,598	62	25	23	80
December.....	840	50,500	1,370	1,474	68	24	23	60

Table 2 indicates the results of operation during the year 1931 on the same group of furnaces. The results of operation for the first five months of 1931 indicate a coke consumption of 1884 lb. per ton of pig iron, with a burden containing 46 per cent sinter. During this period the blast temperature was 1106° F. The production was 760 tons per day and the wind blown was 56,100 cu. ft. The flue dust production was 177 lb. per ton. During the months of September and October of the same year the fuel consumption was 1693 lb. per ton of pig. There were 750 tons of iron produced per day. The blast temperature was 1240° F. and the flue dust production was 82½ lb. per ton. During

September and October the operation was much better than during the first five months of the year. All conditions remained approximately the same except that less wind was blown and higher blast temperatures were used, which resulted in a reduction of coke consumption of about 191 lb. During the months of November and December of the same year the sinter was increased to 65 per cent with practically no change in the amount of air blown. The blast temperature was about 70° higher and the average coke consumption was 1536 lb., or 157 lb. lower than during September and October. The average tonnage produced was 822 tons and there was no increase in flue dust production.

The furnace indicated has a hearth 24 ft. in diameter and is now producing 900 tons per day. It is obvious that if business conditions warranted an increase, the production could be raised to 1100 or 1200 tons of pig iron per day by using the same percentage of sinter in the burden.

The sinter on this furnace contains approximately 59 per cent iron and is produced from flue dust, to which has been added about 25 per cent Mesabi fine ores or mill scale. The sinter was produced on a Dwight-Lloyd sintering machine.

The addition of the fine ores to the flue dust prior to the sintering effected two beneficial results: (1) the elimination of a certain amount of fine ore from the burden; (2) the reduction of carbon in the flue dust. It was found that the capacity of the sintering machine was greatly improved when the carbon content of the charge held within narrow limits.

SOURCE OF SINTER

I have used sinter in an ore mixture for a number of years. The sinters which I have used have been made from Cuyuna Range ore fines. I have also had experience in the use of sinter made from flue dust. I have found that from the standpoint of the operator there is very little difference in the quality of sinter produced from fine ores and that produced from flue dust. Operation with either seems to give the same beneficial effects on the furnace. Both of the sinters have an open, porous structure, are strong and will not crumble and produce any appreciable percentage of fines when handled in the routine of transportation, stocking, charging, etc.

TABLE 3.—*Typical Screen Analysis of Sinter*

SCREEN	PER CENT	SCREEN, MESH	PER CENT
Over 1 in.....	37.71	Through 20 on 40.....	1.18
Through 1 on ½ in.....	20.59	Through 40 on 60.....	0.34
Through ½ on ¼ in.....	22.44	Through 60 on 80.....	0.17
Through ¼ in. on No. 8 mesh....	11.02	Through 80 on 100.....	0.12
Through 8 on 20 mesh.....	6.05	Through 100.....	0.37
			100.00

Table 3 gives a screen analysis of the typical sinter which has been handled five times in the course of manufacture and transportation between the sintering plant and the stock pile. It will be noted that no appreciable amount of fines are present in this sinter. Only 1 per cent of the sinter passed through a 40-mesh screen and 0.37 per cent passed a 100-mesh screen.

BLAST TEMPERATURES

My experience has shown that the use of burdens containing 15 to 40 per cent sinter, with an average over a period of two years of approximately 30 per cent, facilitates the use of high blast temperatures. With each increase in sinter in the furnace burden it was found possible to increase the blast temperature correspondingly.

Table 4 indicates the result of two consecutive months of operation under normal conditions where 23 and 33 per cent of sinter were used in the burden. The use of this sinter decreased the coke consumption some 65 lb. The blast temperature was increased 28 degrees and the ore-coke ratio was increased from 2.21 to 2.28.

TABLE 4.—*Results of Two Consecutive Months of Operation*

Blast Temperature, Deg. C.	Coke, Lb. per Ton	Sinter, Per Cent	Ratio, Ore: Coke
1496	1808	33.0	2.28
1524	1873	23.3	2.21

CONCLUSIONS

It has been noticed that with each increase in sinter with the same amount of wind, an increase in daily tonnage has resulted. This is due in part to the fact that the use of increased amounts of sinter resulted in enrichment of the burden and the reduction of the flue dust produced. As far as the practical operation of the furnace is concerned, it is obvious that the use of sinter gives a burden which is much more readily smelted and more easily handled than a burden composed of raw ore. The result undoubtedly is due to the physical size of the sinter and incidentally to the fact that the iron in the sinter is in the form of magnetite. Blast-furnace operators generally correlate high coke consumption and difficult operation with the use of magnetite, but I believe that this is due mainly to the physical condition of the raw magnetite as charged. In general, magnetite ores are more or less dense and when they are charged in large sizes into the furnace high coke consumption results.

DISCUSSION

(Franklin B. Richards presiding)

F. B. RICHARDS, Cambridge, Mass.—When we were using all Mesabi ores with no preparation, we were limited to a blast temperature of about 970° to 1050° . Higher than that temperature, the furnace stuck and stopped moving. We had to wait and slacken the wind until the stock came down, and this method of changing the composition of the ore burden has given wonderful results. I do not know how high the blast temperature was carried when coarse ores were used but it was 1250° or 1350° or higher. There was an old-fashioned idea that it was impossible to use over 15 to 20 per cent of sinter; but that apparently has been exploded. Mr. McClurkin told me that one of his neighbors had tried up to 80 per cent of sinter in the ore burden with the very best results, and it is a good thing that this has been demonstrated, especially in regard to the future supply from Lake Superior, as in 15 or 20 years from now there will be millions of tons that will have to be produced in this way for blast furnaces.

R. H. SWEETSER, New York, N. Y.—In this paper, and in Mr. Harrison's,³ the fact has been brought out that a sinter is mostly magnetic iron ore or magnetite, and the silicate of iron, and the statement is made that the magnetite is more easily reduced than the hematite. I believe that most of us were taught that magnetite was harder to reduce than hematite, and I wish that this question might be cleared up. Is it a fact that Fe_3O_4 is more easily reduced than Fe_2O_3 ?

Regarding the reduction of silicate, Mr. McClurkin says that it has a lower melting point, but what about the reduction of the silicate? Those of us who have had the experience with mill cinder realize that mill cinder comes way down into the furnace, and is not easily reduced. It probably melts before it is reduced. Is all the advantage of the silicate in sinter due to the fact of its almost perfect physical condition, or is there a chemical reaction that makes it necessary to melt the silicate in the sinter before it is reduced?

F. B. RICHARDS.—You know, Mr. Sweetser, that you can melt a crystal of magnetite with a blowpipe. Did not that happen more or less with the large lumps of magnetite, or before it was reduced did it not get down into the lower zones in the furnace before reduction had taken place, on account of its physical character, large sizes and no preparation?

Sinter, according to these papers, is almost a perfect vehicle for the gases, and there is no evidence that it is not rapidly reduced. I think the evidence of the low fuel would tend to show that those ores have thoroughly reduced; that they are well down in the furnace, and properly prepared for melting in the melting zone.

It is a great advantage to use higher blast temperature, as that helps in the lower fuel.

R. H. SWEETSER.—I agree with Mr. McClurkin and Mr. Harrison 100 per cent. I have been a hard ore smelter a good many times during my experience, and I have always felt that there was an unwarranted prejudice against magnetic iron ores, and I think possibly Mr. McClurkin has just touched on the reason. He says, in general, that magnetite ores are more or less dense, and in cases where they are charged in large sizes into the furnace, high coke consumption results. Well, if big lumps are put into the blast furnace, there will be higher coke consumption. The reports of actual results show that we can get lower coke consumption with properly prepared magnetite ore in the form of sinter than we do with the other ores, but there is a technical ques-

³ See page 57.

tion I wish could be settled. The statement is made in this paper that Fe_2O_3 requires more heat for reduction than Fe_3O_4 . Is that a fact?

W. A. BARROWS, JR., Philadelphia, Pa.—Is not the trouble formerly complained of in smelting magnetites due to presence therein of silicate of protoxide of iron? This compound has a melting point comparatively low, not much above the temperature required to reduce to the metallic state the iron contained in it. Furnacemen used to claim that certain magnetites melted too high in the furnace and by assuming liquid form before entirely reduced caused scouring of the furnace walls and also brought unreduced iron into the hearth, causing irregular working.

Many years ago when large quantities of mill cinder were used at blast furnaces, it was the custom when changing to a cinder mixture from an all ore mixture, to reduce the percentage of ore and cinder below that which had been ordinarily carried of ore only. The volume of air was reduced and the furnace operation slowed up. Mill cinder carries high percentages of the silicate of protoxide of iron.

The reduction of iron in the silicate proceeds much more slowly when the compound becomes liquid and of course nonporous, as the reducing gases can contact the exterior only.

If the sinter is not overburned and too strongly fused, I do not think it will cause the troubles mentioned. In fact, it is beyond question a very satisfactory material for furnace use.

P. G. HARRISON, Ironton, Minn.—Mr. Schwartz says that all sinter contains iron silicate, and I think most of our professors say that iron silicate does not reduce easily. But magnetite ores charged in crude lumps in the eastern practice, I believe, take about 2400 lb. of coke.

F. B. RICHARDS.—Up to 2700 pounds.

P. G. HARRISON.—They ground those magnetite ores and concentrated them, made a concentrate, and sintered the concentrates. Coke dropped down about four, five, or six hundred pounds. When they sintered they made iron silicate, which supposedly will not reduce, but they saved five to seven hundred pounds of coke, and I do not care whether it reduced or not, they made pig iron.

As to blast temperatures—Mr. McClurkin's furnace, using from 20 to 30 per cent of sinter, gets part of its results from the fact that they use very high blast temperatures, 1500° to 1600° , without any difficulty of sticking the furnace. I think the significance is that there is enough sinter so that there is no sticking in the furnace with a high-temperature blast. The economy of sinter lies just about as much in the fact that the blast temperatures can be raised on the furnace as it does in the chemical quality of the sinter. The real saving comes entirely from the structure of sinter. I have an experience on that.

"Sinter Dried," a mixture of coarse ore and sintered ore fines, is something new. It was used this year to the extent of 65 per cent of the burden on a coke furnace in making foundry iron—3 per cent silicon in the iron and $11\frac{1}{2}$ per cent silica in the ore. The coke consumption, as I remember, was a little under 1600 lb.; fine dust about 80; amount of sinter in the sinter dried, about 33 per cent. These results are as good, I believe, as can be found any place with higher sinter. This is because of the structure of sinter-dried ore, which is all lump ore and sinter of perfect structure.

The reducibility of the individual ore or sinter particles in a test tube or before a blow torch I do not believe is important. Throw it in the blast furnace, and if the coke consumption comes down, that is all that is necessary.

C. E. WILLIAMS, Columbus, Ohio.—Sufficient study has been made of the relative rates of reduction of magnetite and hematite to show that a longer time is required for

the reduction of natural magnetite to metal than for hematite or limonite. The slower rate of reduction of magnetite probably is the result of a physical rather than a chemical effect. As the reduction of iron oxides is accomplished by carbon monoxide which must diffuse through the ore particles for complete reduction, the denser ore particles will require a longer time for complete reduction.

Artificial magnetite formed by the partial reduction of hematite requires about the same length of time for reduction as hematite. Sinter would reduce at about the same rate as other forms of iron oxide of similar structure, regardless of whether the iron were present as Fe_2O_3 or Fe_3O_4 . Small differences in the rates of reduction of different forms of iron oxide exist perhaps, but I believe that aside from the effect of density these are not sufficiently great to make important differences in the blast-furnace operation.

The effect of size distribution of the blast-furnace charge has such a large effect upon the rate of reduction of the ore that this factor is of more importance, I believe, than the condition in which the iron exists in the sinter. In other words, the use of well sized sinter and of properly sized charges to the furnace result in such important improvements in blast-furnace operations as to mask the effect of the slight difference in rate of reducibility of sinters in which the iron is in different states of oxidation.

Our analyses of sinters made by different processes show that the amount of magnetite varies a great deal. Some showed that one-half the iron was present as Fe_2O_3 and one-half as Fe_3O_4 , others a relatively small amount of Fe_2O_3 , and still others contained more FeO than is accounted for by Fe_3O_4 . The tests indicated a small amount of iron silicate in all sinters examined. The amount, however, was so small as to have little effect on the reducibility of the entire piece of sinter.

In conclusion, I consider that the large saving in coke effected by simply changing the range of size of the charge has such a great effect upon the blast-furnace operation as to make consideration of the reducibility of different forms of iron, except for the natural magnetites, of little practical importance.

B. S. STEPHENSON, New York, N. Y.—I happen to know something of the furnace which Mr. McClurkin operates, and know that it is quite usual for that furnace to run for a year with practically no off casts—that is, not over two or three casts which are off grade from the standpoint of sulfur, silicon or any other essential characteristic, indicating its smooth operation. Its charts indicate the steadiest, smoothest sort of flow; there is no checking or slipping, or anything of that kind. In fact, furnace practice is almost ideally perfect on that sort of mixture.

Sintering Economics

By PERRY G. HARRISON,* IRONTON, MINN.

(New York Meeting, February, 1932)

THE increased use of sintering for the beneficiation of iron ores and the reclaiming of flue dust creates a lively interest in sintering costs and economics. The character of material sintered and geographical location of plants so radically alter sintering costs and economics that it is well to understand at least the basic elements which control such changes.

The following cost factors are believed to be roughly approximated for large-scale Dwight-Lloyd continuously operated sinter-machine installations located anywhere.

	PER CRUDE TON
Labor, supplies and repairs	0.15
Power 6.5¢ × kw-hr. rate	?
Plant overhead and administration	0.05
Depreciation per ton annual capacity	0.05
Fuel:	
6 per cent coke breeze or equivalent minimum	?
1 per cent coke breeze additional for each 5 per cent free and combined water in ore or dust	?
Ignition distillate at 0.6 gal. per ton	?

	PER SINTER TON
Royalty on ore	0.10
Royalty on flue dust	0.15

	PER CRUDE TON
"Winter expense"; i. e., the cost of the five months enforced idle period for plants tied in to Great Lakes transportation season	0.03

Using the foregoing data, it is possible to roughly approximate the cost of efficient sintering at any location for any ore, viz:

	PER CRUDE TON HANDLED	PER TON SINTER
1. <i>Flue Dust—Steel Plant Locations</i>		
Sinter recovery, 15 per cent moisture and carbon		85 per cent
Labor, supplies and repairs	0.15	0.18
Power 6.5¢ × 1¢ kw-hr.	0.065	0.08
Plant overhead and administration	0.05	0.06
Depreciation per ton	0.05	0.06
Dust handling and preparation	0.10	0.12
Fuel: free, contained in dust		
Ignition: blast-furnace gas free		
Royalty		0.15
<i>Total</i>		<u>\$0.65</u>

Note:—Cost increased by either deficiency or considerable excess of carbon in dust.

* General Manager, Evergreen Mining Co.

	PER CRUDE TON HANDLED	PER TON SINTER
2. Magnetite Ore Concentrate—Pennsylvania and New York Locations		
Sinter recovery, 4 per cent moisture	96 per cent	
Labor, supplies and repairs	0.15	0.16
Power 6.5¢ × 1¢ kw-hr.	0.065	0.07
Plant overhead and administration	0.05	0.05
Ore preparation: None; i.e., delivered on belt from concentrator		
Depreciation per ton	0.05	0.05
Fuel		
$1\% \times \frac{4\%}{5\%} = .8$		
$6.8\% \times \$2.50$	0.17	0.18
Ignition: oil 0.6 × 7¢	0.04	0.04
Royalty		0.10
Total		\$0.65

3A. Cuyuna Range Ore—Mine Plant

Sinter recovery, 25 per cent moisture, free and combined	75 per cent	
Labor, supplies, and repairs	0.15	0.20
Power 6.5¢ × 1.5¢	0.10	0.13
Plant overhead and administration	0.05	0.07
Ore preparation	0.10	0.13
Depreciation $0.05 \times \frac{12}{7}$ month active	0.09	0.12
Fuel $1\% \times \frac{25\% \text{ moisture}}{5\%} = 5\%$		
6%		
$11\% \times \$4.10$ per ton	0.45	0.60
Ignition: oil 0.6 gal. × 7¢	0.04	0.05
Royalty		0.10
Winter expense	0.03	0.04
Total Sintering Cost	\$1.44	\$1.44

3B. Cuyuna Range Ore—Shipped and Sintered at Steel Plant

Sinter recovery, 25 per cent moisture, free and combined	75 per cent		
Labor, supplies and repairs	0.15	0.20	0.20
Power 6.5¢ × 0.8¢	0.05	0.07	0.07
Plant overhead and administration	0.05	0.07	0.07
Ore stocking and reclaiming	0.10	0.13	0.13
Depreciation	0.05	0.07	0.07
Fuel— $11\% \times \$1.00$	0.11	0.15	0.00
Ignition: blast-furnace gas free			
Royalty		0.10	0.10
Sintering Cost Only	\$0.79	\$0.64	

MIXED WITH
FLUE DUST;
i. e.,
FREE FUEL

	PER CRUDE TON HANDLED	PER TON SINTER	MIXED WITH FLUE DUST; i. e. FREE FUEL
<i>Additional Mining and Freight Costs</i>			
Ore crushing and preparation	0.10	0.13	0.13
Royalty $\frac{60¢}{75\%} = \$0.80 - \$0.60$		0.20	0.20
Freight $\frac{\$1.79}{75\%} = \$2.39 - \$1.79$		0.60	0.60
<i>Total Additional Cost</i>		<u>\$0.93</u>	<u>\$0.93</u>
<i>Lake Front Furnace Equivalent Cost</i>		<u>\$1.72</u>	<u>to \$1.57</u>
Shipped to Pittsburgh District			
Additional Freight $\frac{\$1.23}{75\%} = \$1.64 - \$1.23$		0.41	0.41
<i>Interior Furnace Equivalent Cost</i>		<u>\$2.13</u>	<u>\$1.98</u>
<i>Mine Sinter Plant Advantage over Lake Front Furnace Plant</i>		\$0.28	to \$0.13
<i>Mine Sinter Plant Advantage over Interior Furnace Plant</i>		\$0.69	to \$0.54
<i>Lake Front Plant Advantage over Interior Furnace Plant</i>		\$0.41	to \$0.41

The foregoing cost analysis illustrates the fact that, while sintering at a mine is far more costly than at a steel plant, the extra cost is far over-balanced in the case of high-moisture ores by savings effected by reason of the reduction in bulk of product to be shipped. A manganiferous ore having only a 71 per cent weight recovery on sintering will show greater advantages than indicated in the above tabulation.

4A. Mesabi Range High-grade Ore Fines—Sintered at Mine	PER CRUDE TON HANDLED	PER TON SINTER
Sinter recovery, 15 per cent moisture, free and combined		85 per cent
Labor, supplies and repairs	0.15	0.18
Power 6.5¢ × 1.5¢ kw-hr.	0.10	0.12
Plant overhead and administration	0.05	0.06
Ore preparation	0.10	0.12
Depreciation $0.05 \times \frac{12}{7}$ month active	0.09	0.11
Fuel $\frac{15}{5\%} = 3\%$		
6%		
9% × \$4.10 ton	0.37	0.43
Ignition: oil 0.6 gal. @ 7¢	0.04	0.05
Winter expense	0.03	0.04
Royalty		0.10
<i>Total Sintering Cost</i>		<u>\$1.21</u> <u>\$1.21</u>

These costs 12¢ less if fines are delivered over belt from concentrator; i. e., ore preparation cost.

	PER CRUDE TON HANDLED	PER TON SINTER	MIXED WITH FLUE DUST; i. e., FREE FUEL
4B. Mesabi Range High-grade Ore Fines—Shipped and Sintered at Steel Plant			
Sinter recovery, 15 per cent moisture, free and combined		85 per cent	
Labor, supplies and repairs	0.15	0.18	0.18
Power 6.5¢ × 0.8¢ kw-hr.	0.05	0.06	0.06
Plant overhead and administration	0.05	0.06	0.06
Ore stocking and reclaiming	0.10	0.12	0.12
Depreciation	0.05	0.06	0.06
Fuel 9% × \$1.00	0.09	0.11	0.00
Ignition: blast-furnace gas free		0.00	0.00
Royalty		0.10	0.10
<i>Sinter Cost Only</i>		<u>\$0.69</u>	<u>\$0.58</u>
<i>Additional Mine and Freight Cost</i>			
Ore crushing and preparation	0.10	0.12	0.12
Royalty $\frac{60¢}{85\%} = 0.71 - 0.60 =$		0.11	0.11
Freight $\frac{\$1.79}{85\%} = \$2.10 - \$1.79 =$		0.31	0.31
<i>Total Additional Cost</i>		<u>\$0.54</u>	<u>\$0.54</u>
<i>Lake Front Furnace Equivalent Cost</i>		<u>\$1.23</u>	<u>\$1.12</u>
Shipped to Pittsburgh District			
Additional freight $\frac{\$1.23}{85\%} = \$1.45 - \$1.23$		0.22	0.22
<i>Interior Furnace Equivalent Cost</i>		<u>\$1.45</u>	<u>\$1.34</u>
<i>Mine Sinter Plant Advantage over Lake Front Furnace Plant</i>		\$0.02 to	\$-0.09
<i>Mine Sinter Plant Advantage over Interior Furnace Plant</i>		\$0.24 to	\$0.13
<i>Lake Front Furnace Plant Advantage over Interior Furnace Plant</i>		\$0.22	\$0.22

The foregoing cost analysis shows that Mesabi ore fines having only 15 per cent free and combined moisture and, therefore, a similar reduction of bulk in sintering can probably be sintered with equal advantage at either Lake front steel plant or at mine.

	PER CRUDE TON HANDLED	PER TON SINTER
5A. Eastern Mesabi or Other Lake Superior Magnetite Concentrates—Sintered at Mines		
Sinter recovery, 10 per cent moisture in concentrates		90 per cent
Labor, supplies and repairs	0.15	0.17
Power 6.5¢ × 1.0¢ kw-hr.	0.065	0.07
Plant overhead and administration	0.05	0.06
Ore preparation, delivered free on belts	0.00	0.00
Depreciation $0.05¢ \times \frac{12}{7}$ month active	0.09	0.10

Fuel $\frac{10\%}{5\%} = 2\%$ fuel	PER CRUDE TON HANDLED	PER TON SINTER
6% fuel		
8% fuel $\times \$4.10$ ton	0.33	0.37
Ignition: oil 0.6 gal. $\times 7\text{¢}$	0.04	0.04
Winter expense	0.03	0.03
Royalty		0.08
<i>Total Sintering Cost</i>		<u>\$0.92</u> <u>\$0.92</u>

5B. <i>Eastern Mesabi or Other Lake Superior Magnetite Concentrates—Sintered at Steel Plants</i>			MIXED WITH FLUX DUST; i. e., FREE FUEL
Sinter recovery, 10 per cent moisture in concentrates	90 per cent		
Labor, supplies and repairs	0.15	0.17	0.17
Power $6.5\text{¢} \times 0.8\text{ kw-hr.}$	0.05	0.06	0.06
Plant overhead and administration	0.05	0.06	0.06
Ore stocking and reclaiming	0.10	0.11	0.11
Depreciation	0.05	0.06	0.06
Fuel 8% $\times \$1.00$	0.08	0.09	0.00
Ignition: blast-furnace gas free	0.00	0.00	0.00
Royalty		0.10	0.10
<i>Sintering Cost Only</i>		<u>\$0.65</u>	<u>\$0.56</u>
<i>Additional Mining and Freight Costs</i>			
Royalty, ? Low, Adjustment Small		?	?
Freight $\frac{\$1.79}{90\%} = \$1.99 - \$1.79$		\$0.20	\$0.20
<i>Total Additional Cost</i>		<u>\$0.20</u>	<u>\$0.20</u>
<i>Lake Front Furnace Equivalent Cost</i>		\$0.85	\$0.76
Shipped Pittsburgh district			
Additional freight $\frac{\$1.23}{90\%} = \$1.37 - \$1.23$		0.14	0.14
<i>Interior Furnace Equivalent Cost</i>		<u>\$0.99</u>	<u>\$0.90</u>
<i>Lake Front Furnace Plant Advantage over Mine Sinter Plant</i>		\$0.07	\$0.16
<i>Mine Sinter Plant Advantage over Interior Furnace Plant</i>		\$0.07	\$-0.02
<i>Lake Front Furnace Plant Advantage over Interior Furnace Plant</i>		<u>\$0.14</u>	<u>\$0.14</u>

The foregoing cost analysis illustrates the advantage of sintering low-moisture ore fines or concentrates at Lake front furnace steel plants over mining plant location.

Conclusion can be reached that, under present conditions, Lake Superior ores carrying less than 15 per cent moisture are sintered more economically at Lake front steel plants; over 15 per cent moisture, at mine sintering plant; never at interior furnace plants.

Ore-sintering costs, although not high as compared to many metallurgical processes, are however very high as compared to the value of the material treated or to the familiar low-cost ore-washing process. Any improvement or modification of the process that will result in materially lower costs and yet retain advantages is important. There are two principal reasons for sintering ore; first, and by far the most important,

improvement in structure; second, and of less importance, reduction in bulk by elimination of moisture or other volatiles. No modification of the process is possible with flue dust or with ore concentrate fines, as the structure of these materials is 100 per cent bad. Most natural crude ores requiring sintering, however, are a mixture of high-moisture fines and coarse ore containing less moisture. These two constituents can be separated by screening, and the coarse ore, usually limonitic hematite of easy reducibility and perfect structure, can be shipped and used direct in furnace; the fines only requiring sintering. This process is feasible and has been used to advantage, although there are some difficult grading problems involved because there is a constant wide variation in relative quantity of coarse and fines and their analyses.

During 1931, the Evergreen Mining Co. (a predecessor of the Evergreen Mines Co.), developed the "sinter dried" process which meets the requirement of lower costs while still retaining the structural advantages of the sintering process.

The "sinter dried" process consists of first crushing an ore so as to eliminate all large lumps and boulders, passing the crushed product over screens with about $\frac{1}{4}$ -in. opening which separates the coarse ore from the fines; the fines are sintered and the hot resultant sinter recombined with the coarse ore. The heat of the sinter drives off part of the superficial moisture from the coarse ore; *i.e.*, the ore is "sinter dried." The structure of sinter-dried aggregate is ideal, *viz.*,

Typical Screen Test of Sinter-dried Ore

Crowell & Murray Average on 103,029 Tons Sampled at Lake Erie Ports

	Per Cent per Screen	Accumulative Per Cent
+ $\frac{1}{8}$	79.2	79.2
+20	8.1	87.3
40	5.0	92.3
60	2.5	94.8
80	.6	95.4
100	.9	96.3
Through 100	3.7	100.0

Sinter drying gives a complete control of iron analysis as the percentage of material passed through the fine screens and sintered can be varied at will with screen size and the iron analysis raised or lowered by such changes in the proportion sintered. The ratio of elements, aside from water, in the sinter and crude ore comprising a sinter dried product is uniform, the sinter merely being a more concentrated form of the ore than is the coarse ore with which it is mixed.

Another method of reducing ore-sintering cost has made great strides recently at Buffalo, where Mahoning ore is screened and the fines mixed

with flue dust having an excess carbon content sufficient to sinter a large percentage of such ore fines. Not only does this mixing result in a low cost for sintering the ore, but also reduces the cost of sintering the flue dust, by reason of the fact that any excess of carbon in flue dust over that required to sinter it increases costs both by reason of excessive machine and grate-bar repairs and because of reduced machine capacity.

The cost of sintering and the relation of such cost to location and type of ore as set out in this paper gives only one of three sides of the picture of sintering economies. The economies effected by the reclamation of large quantities of worthless flue dust and the beneficiation of low-silica, low-iron, high-moisture, poor-structure iron ores and of finely ground concentrates form a second side of the picture. The third, and possibly most important side, is the possible effect of the use of sinter, or sinter-dried ore, on blast-furnace economy.

Blast furnaces are charged with carefully prepared coke, carefully sized and cleaned limestone and then choked full of dust-forming, gas-draft-passage-blocking ore fines. It is intriguing to consider tonnage and operating possibilities to be expected when some big, 20-ft. furnace is charged not only with good coke and clean limestone but also with an ore charge made up entirely of cleaned, easily reduced, coarse limonitic ore and sinter, either in the form of sinter-dried ore or as separate charges of coarse ore and sinter.

DISCUSSION

(Franklin B. Richards presiding)

MEMBER.—Mr. Harrison compares the costs of sintering, on the range and at the lower lake ports. One of the difficulties, I believe, is that the fine ores from some of the washing plants could not be easily transported. How would you get the concentrates to the docks?

P. G. HARRISON.—I think there will be difficulty, but the question of shipping fine limonite has come up. Limonite fines can be shipped, but a hard hematite fine or granular concentrate of magnetite type might pour through everything we have now at the docks, just like sand in an hourglass.

We sinter for two large steel companies, and both have compared their costs with ours, and ours are high, but by the time we take credit for the freight and royalties which are saved we can make a profit from sintering their fines at an over-all cost saving to them.

Research on Blast-furnace Slags*

A PROGRESS REPORT

BY RICHARD S. McCAFFERY, MADISON, WIS.

(New York Meeting, February, 1931)

A RESEARCH on iron blast-furnace slags has been in progress since 1922 in the metallurgical department of the University of Wisconsin, supplemented by observations, tests and critical examination of operating records at 10 furnaces. From the data thus collected information has been put into forms suitable for use by furnace operators and is given in this report and the three accompanying papers.¹

In the viscosity results reported, it is estimated that temperatures were measured within $\pm 5^{\circ}$ C. and that the viscosity determination of the particular slag investigated is accurate within ± 4 per cent. In the viscosity diagrams in the various papers, the equal viscosity lines were drawn in such a manner that in all cases they are located correctly with respect to the actual experimental results, but when determining a viscosity for a particular composition from the diagrams, the viscosity may be slightly less accurate than the experimentally determined viscosity for the same slag, for the reason that the iso-vis lines interpolated between the experimental results may be shifted slightly without violation of the experimental data. The viscosity diagrams represent our judgment of their position under the above conditions, and we believe the relative accuracy of viscosity data taken from the diagrams is more than sufficient for any use to which the data may be put.

Hundreds of samples of slags synthetically produced in the laboratory and of actual furnace slags have been studied in various ways. The ranges of compositions of slags used for viscosity measurements are: silica 25 to 55 per cent.; alumina 0 to 35 per cent.; lime 25 to 55 per cent.; magnesia 0 to 20 per cent. These measurements were made at temperatures of 1250°, 1300°, 1350°, 1400°, 1450°, 1500°, 1550°, 1600° and 1650° Centigrade.

Descriptions of apparatus, methods used and statements of the problems investigated have been published in the papers listed in the bibliography beginning on page 120.

* Conducted with the aid of the American Institute of Mining and Metallurgical Engineers, Engineering Foundation and several companies that own blast furnaces. Originally printed as the first paper in *Tech. Pub.* 383.

¹ The three papers referred to are the two papers following this (pp. 86 and 122), which originally formed a part of *Tech. Pub.* 383, and *Tech. Pub.* 384, which was reprinted in *Trans. A. I. M. E.* (1931) 95, Iron and Steel Div., 60-71.

Our apparatus for viscosity determination consists essentially of an induction furnace within which is placed a crucible so supported that it may be rotated at constant speed. This crucible contains the slag of which the viscosity is to be determined. When the slag is molten, a graphite spindle is immersed in it. This spindle is suspended by a spring filament and is carefully centered. When the crucible containing the molten slag is rotated within the furnace at constant speed, the slag tends to drag the spindle around and displace it angularly with respect to its original position in the molten slag. A viscous slag will drag the spindle through a greater angle than will a fluid slag, and this may be made a measure of the viscosity. Details of apparatus and method are given in detail in the second paper of this series: Determination of Viscosity of Iron Blast-furnace Slags. (See page 86.)

COMMENTS ON RESULTS

Broad generalizations for application to all iron slags and to all furnace conditions are impossible. It is the author's belief, nevertheless, that information will be found in this report applicable to any slag that will occur in blast-furnace practice.

Perhaps the most noticeable thing in our work is the effect of magnesia in reducing the viscosity of the slags. The slags without magnesia content are the most viscous. As the magnesia content increases the viscosity decreases at a fairly rapid rate. When slags have a magnesia content of from 15 to 20 per cent., there are no great differences in viscosity at any one temperature with considerable changes in the silica-lime-alumina components. Moreover, in this same range of components (15 to 20 per cent. magnesia) the actual viscosity is only one-sixth or one-eighth the viscosity if no magnesia or only a small percentage of magnesia is present.

To illustrate some of these variations, a series of diagrams (Figs. 1 to 13) at various temperatures with constant 35 per cent. silica content are shown, also a similar series with constant 15 per cent. alumina and another with constant 8 per cent. magnesia.

Comparing generally the slags of 15 to 20 per cent. magnesia with those of little magnesia, although the high-magnesia slags are much less viscous at any temperature, there is also another thing that is very noticeable. If the composition in silica-lime-alumina of the high-magnesia slags is changed at any one temperature, a relatively small change in viscosity results, but if the same change in silica-lime-alumina be made in a low-magnesia slag at the same temperature, a considerable change in viscosity may take place. This change is progressive continuously from the low-magnesia to the high-magnesia slags.

This is probably a matter of great importance. It would be likely to mean in the operation of blast furnaces that the higher magnesia

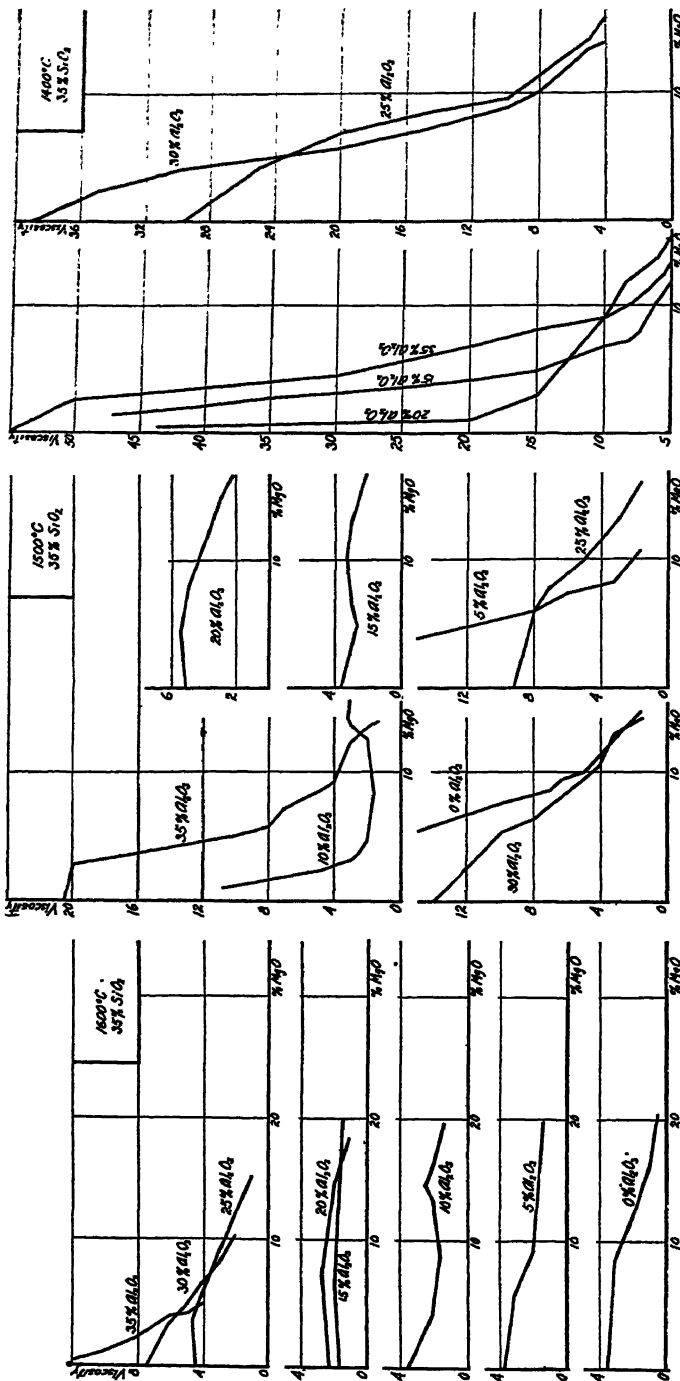


FIG. 1.

Figs. 1 to 7 show the effect of magnesia on the viscosity of slags with various constants.

Figs. 8 to 13 show the effect of alumina on the viscosity of slags with various constants.

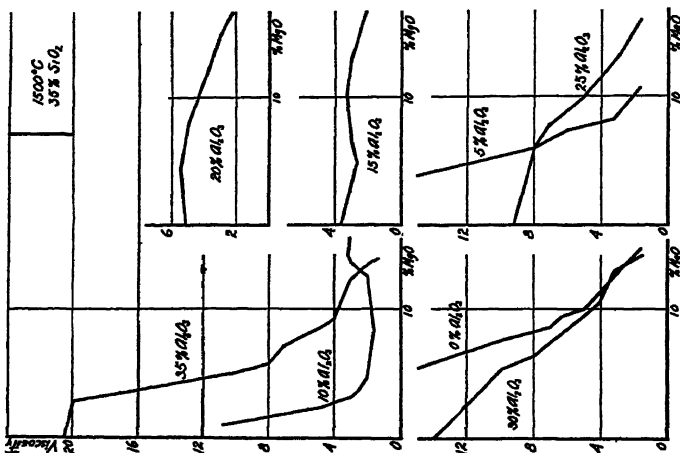


FIG. 2.

Figs. 1 to 7 show the effect of magnesia on the viscosity of slags with various constants.

Figs. 8 to 13 show the effect of alumina on the viscosity of slags with various constants.

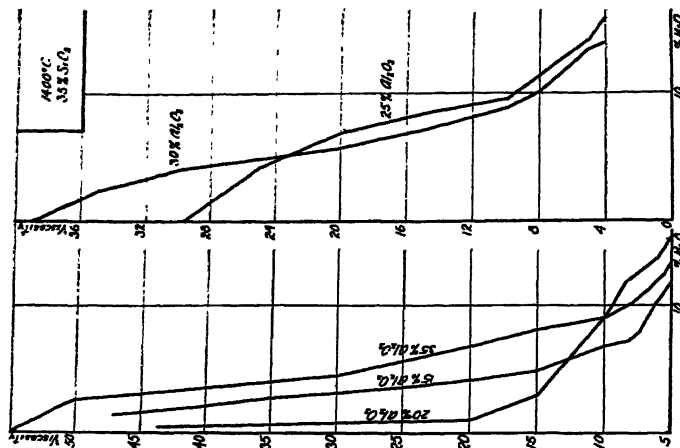


FIG. 3.

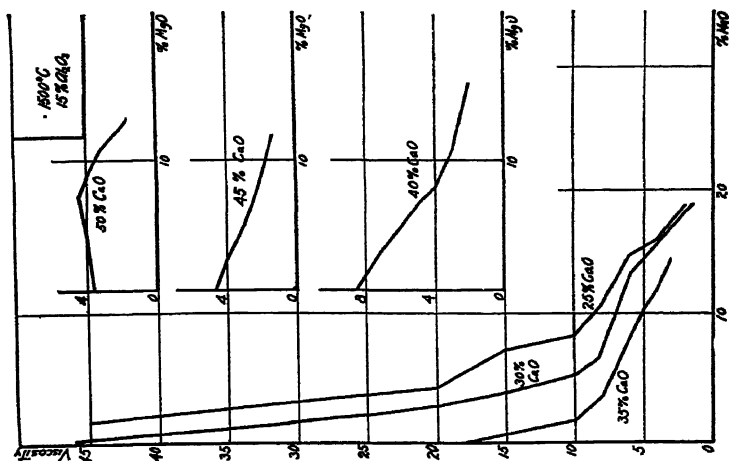


Fig. 6

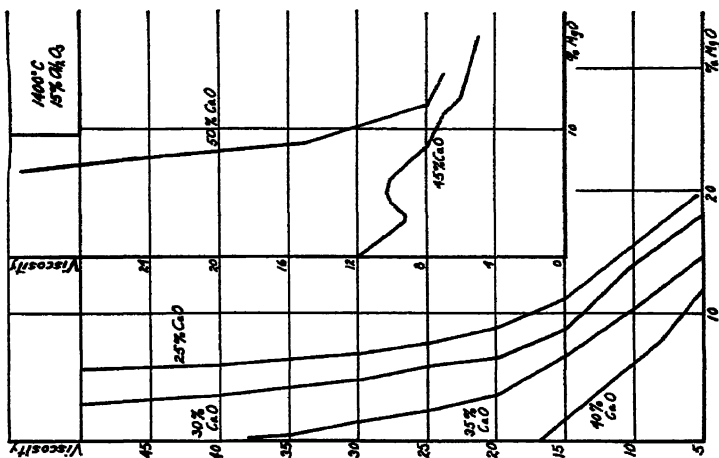


Fig. 5.

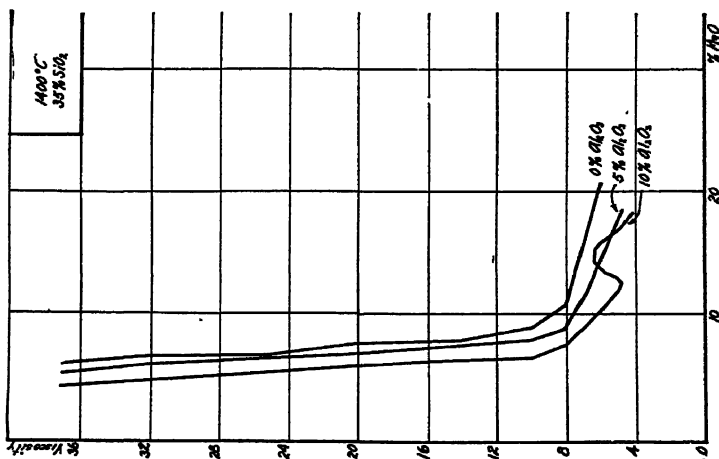


Fig. 4.

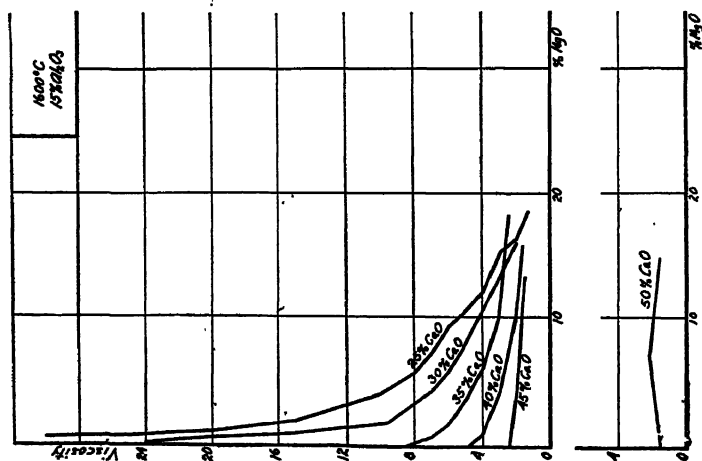


Fig. 7.

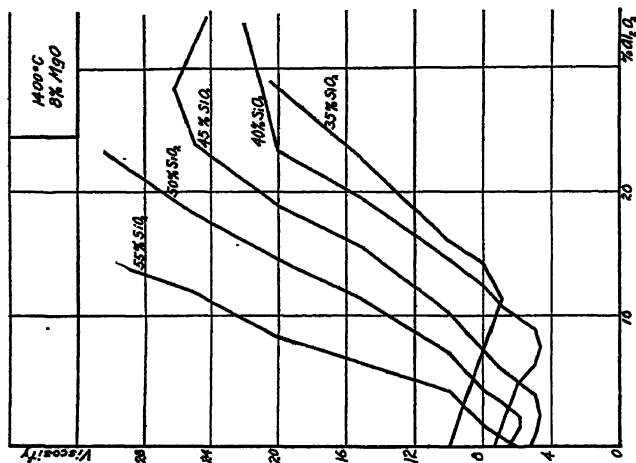


Fig. 8

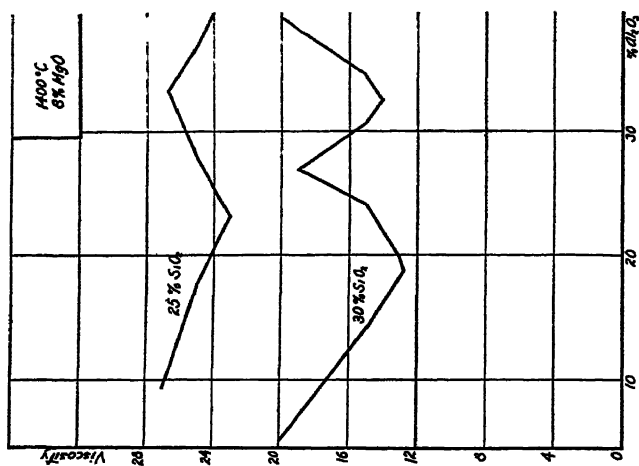


Fig. 9.

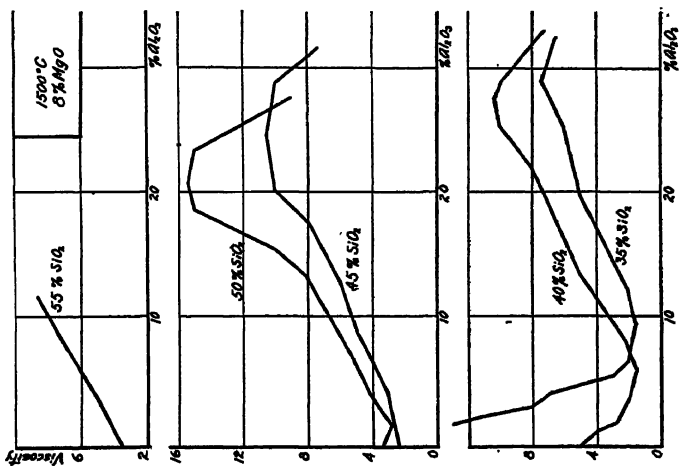


Fig. 10.

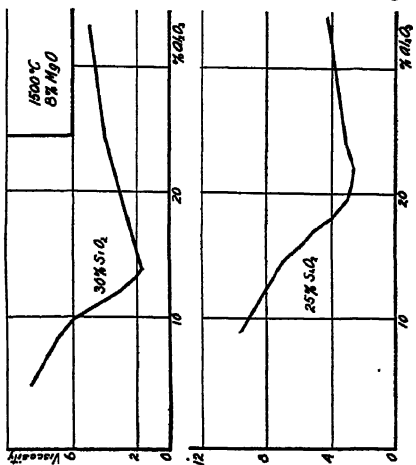


Fig. 11.

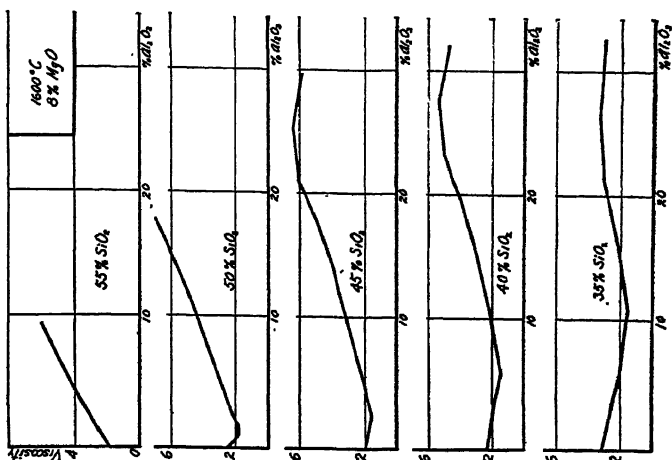


Fig. 12.

slags gave less variation in properties than those of low magnesia content. As the property, viscosity, is bound up complexly with the desulfurizing action of the furnace, it would seem that the use of high-magnesia slags would at least stabilize the desulfurizing function of the furnace and lead to greater regularity of operation.

Whatever be the economic limit of the magnesia content of the slag that may be set, there are certain limits of silica-lime-alumina composition in which viscosity changes are more gradual than in other ranges of silica-lime-alumina composition with the same magnesia. If these ranges are selected, a greater regularity of desulfurizing function will result at these most economical magnesia ranges of composition.

This possibility of greater regularity of furnace operation has not been brought out before by others, so far as the author is aware, but it is one of the definite results from our work.

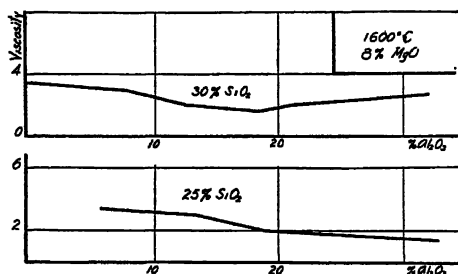


FIG. 13.

Results of this research also make possible accurate determinations of the relative values of the different slag components with respect to their fluxing quality. Quite definitely our work shows that magnesia has much more influence in reducing slag viscosity than has lime. This statement is true in all the ranges of composition in which slags have been made in the past or are likely to be made in the future. There has been and still is considerable discussion of the relative merits of lime and magnesia as flux and even now the old method of adding to the lime content, the lime equivalent of the magnesia present, and considering the total as lime, still persists. The viscosity is certainly part of what is called "fluxing quality," and our work definitely shows that magnesia is quite different from lime in its effect on this property.

When reviewing the literature, it is astonishing to observe the diversity of opinion that has been expressed as to the effect of magnesia in slags. Every statement made by one writer can be contrasted with one diametrically opposed by someone else. The results of our work have cleared up some of these differences.

It is not only possible to make qualitative statements about slag composition from our results, but whenever it may be desirable to make

more accurate or quantitative comparisons as to the economic desirability of either one of two slags, the data are now available.

DATA IN FORMS FOR USE

For detailed use in furnace operation or in other investigations, results of this research to date are summarized in diagrams and tables in this report and in the other two papers printed in this series—*Determination of Viscosity of Iron Blast-furnace Slags* and *The Effect of Magnesia on Slag Viscosity*. (See pages 86 and 122.)

In all diagrams and tables viscosity is expressed in units of viscosity, poises, and temperatures in degrees Centigrade. The compositions include regions beyond those employed in any commercial blast-furnace operation.

In going over the diagrams, it will be observed that there are many fields of composition wherein there are exhibited decided trends. Adjacent to the given fields of composition, there are others in which the trend is just as decided but varies in amount and direction. This is as it should be, and as a consequence broad generalizations applying to all blast-furnace slags are impossible; but any particular slag can be located on the diagrams and by the methods to be outlined in later paragraphs, the effects of changes of composition and temperature on viscosity can be determined readily.

Five series of diagrams give the results of the Wisconsin viscosity determinations on blast-furnace slags:

Series I. Viscosity in terms of the silica-lime-alumina compositions, with magnesia varying 5 per cent. from diagram to diagram, for temperatures 1400°, 1500° and 1600° C. See Figs. 4 to 18 of the third paper in this series (pp. 126-129).

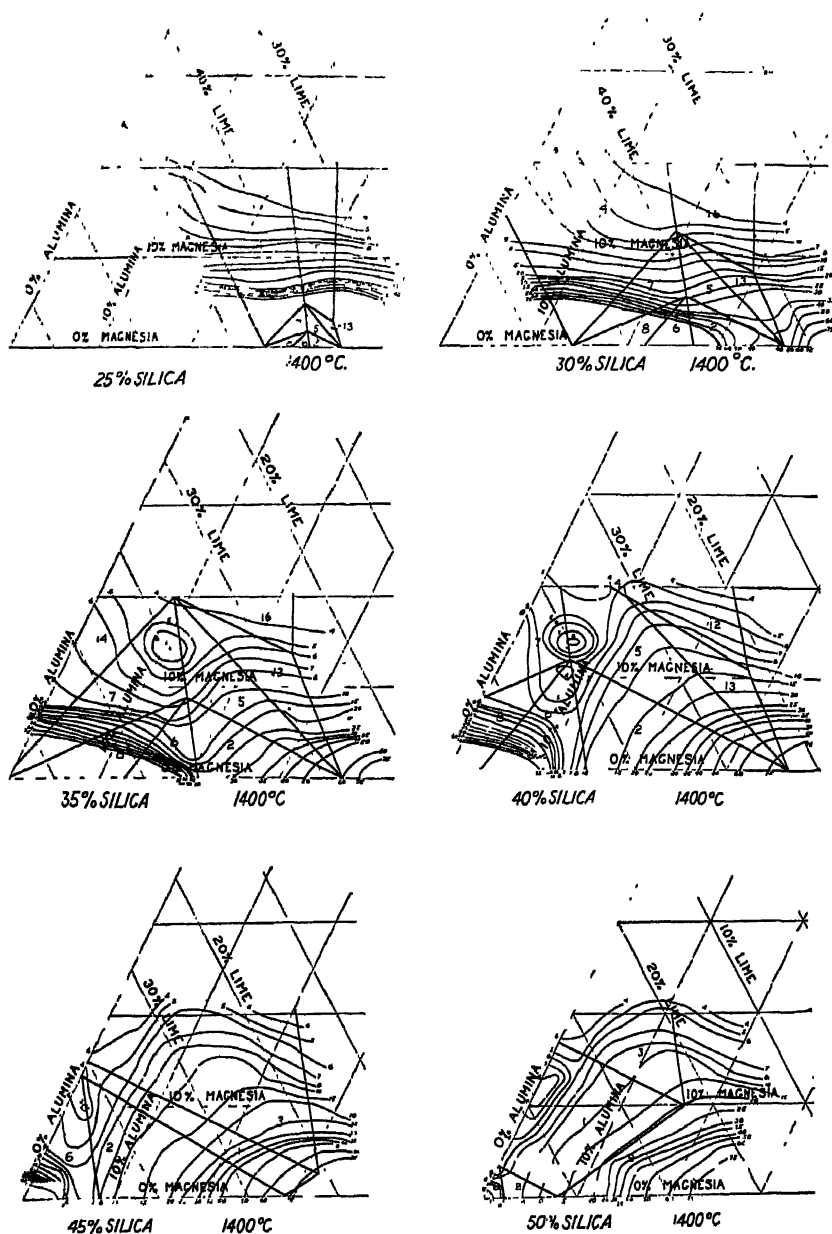
Series II. Viscosity of alumina-lime-magnesia compositions, with silica varying 5 per cent. See Figs. 14 to 34 in this report.

Series III. Viscosity of silica-alumina-magnesia compositions, with lime varying 5 per cent. See Figs. 35 to 55 in this report.

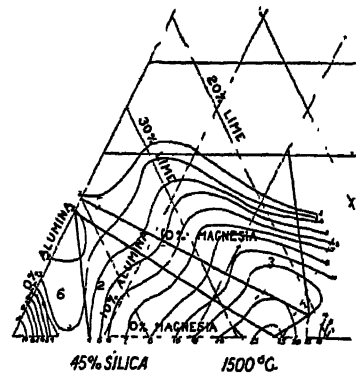
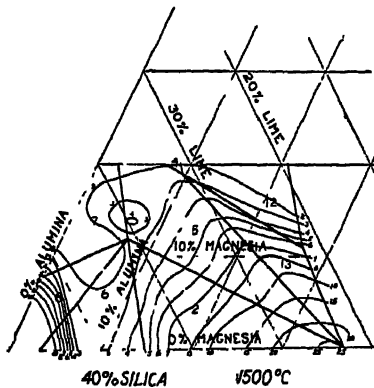
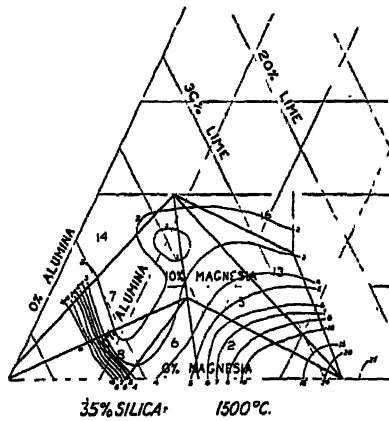
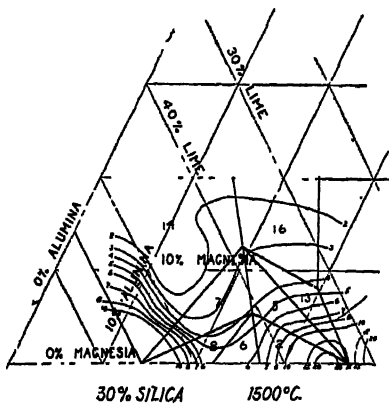
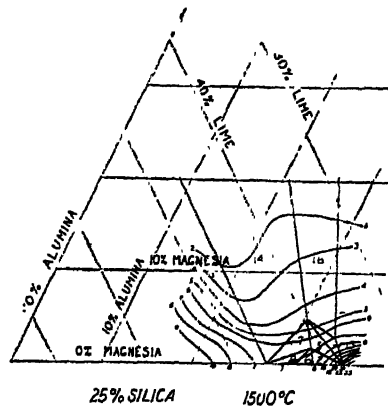
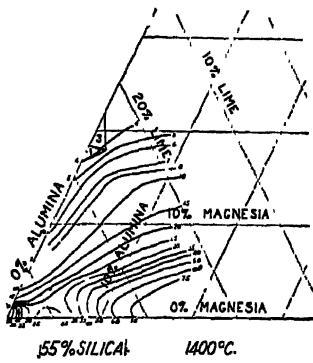
Series IV. Viscosity of lime-magnesia-silica compositions, with alumina varying 5 per cent. See Figs. 56 to 79 in this report.

Series V. Similar to Series I except that viscosity is represented at 1400°, 1500° and 1600° C. (instead of at one selected temperature), in order to show the effect of change of temperature on viscosity in one diagram. See Figs. 19 to 23 of the third paper in this series (pp. 129-130).

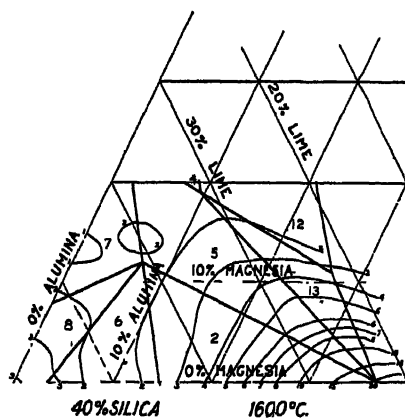
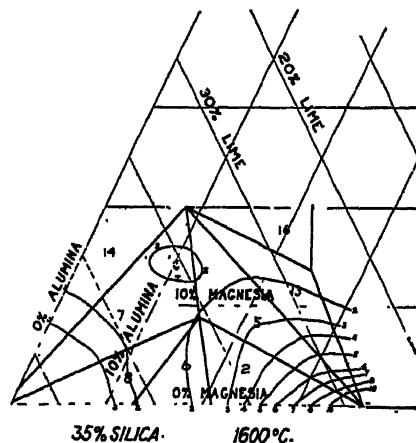
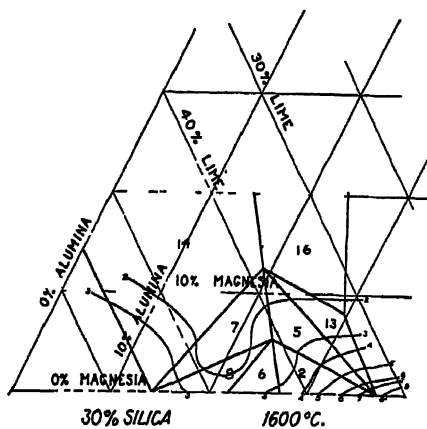
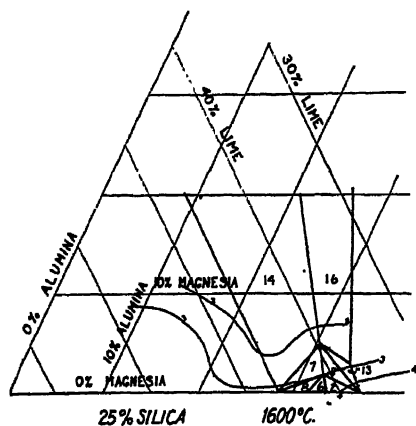
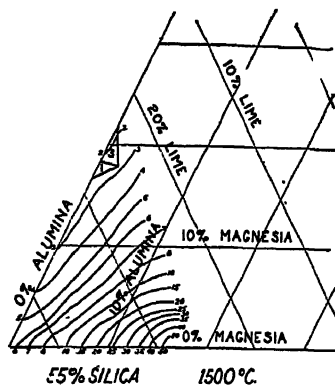
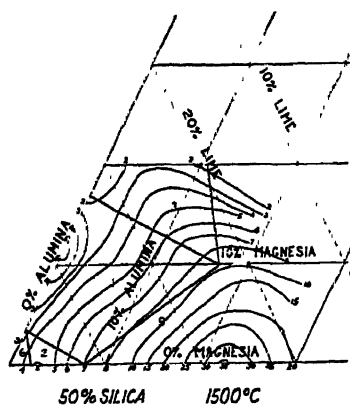
Similar diagrams for intervals of 1 per cent. have been drawn. They can be published whenever there is sufficient demand and provision can be made for the expense. For persons using the results of the Wisconsin investigations in the practical control of blast furnaces, these additional diagrams would be invaluable. There also remain unpublished in dia-



FIGS. 14-19.—VISCOSITY OF ALUMINA-LIME-MAGNESIA COMPOSITIONS WITH SILICA VARYING 5 PER CENT.



FIGS. 20-25.—VISCOSITY OF ALUMINA-LIME-MAGNESIA COMPOSITIONS, WITH SILICA VARYING 5 PER CENT.



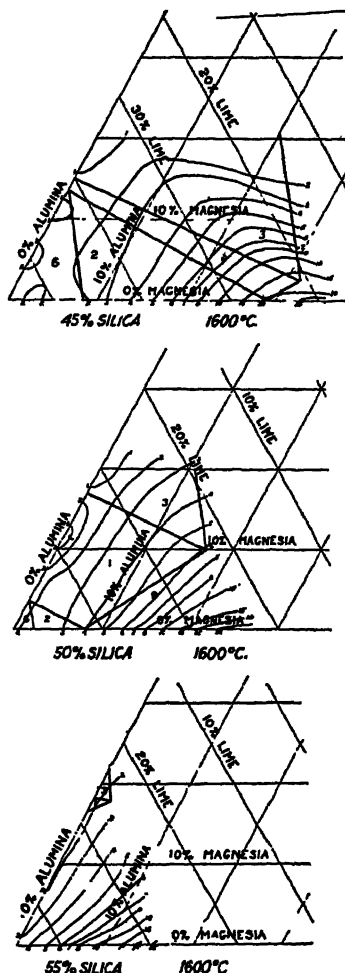
FIGS. 26-31.—VISCOSITY OF ALUMINA-LIME-MAGNESIA COMPOSITIONS, WITH SILICA VARYING 5 PER CENT.

grammatic form, to this date, the data on slag viscosities at temperatures of 1300°, 1350°, 1450° and 1550° Centigrade.

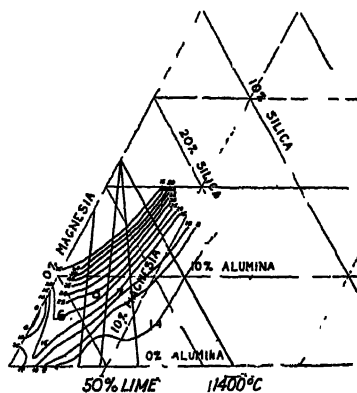
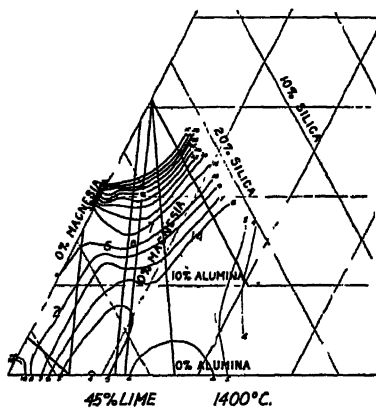
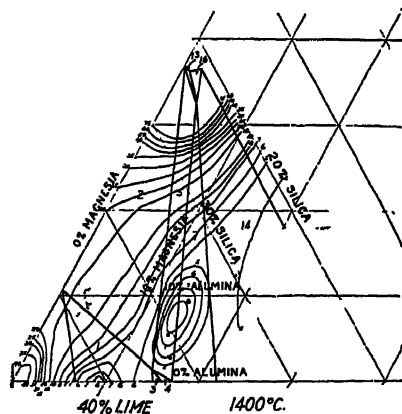
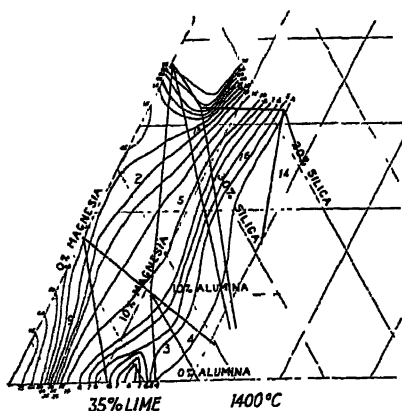
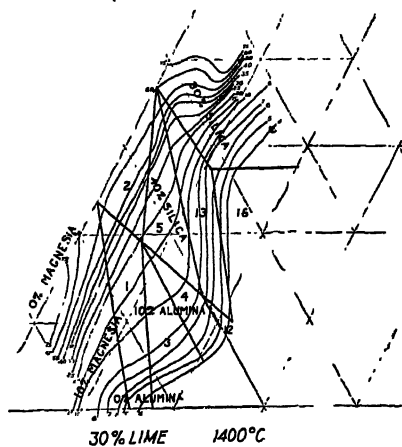
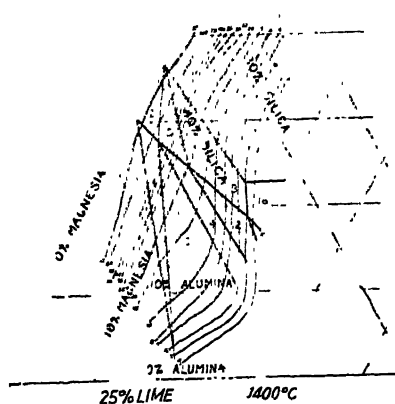
To make the interpretation of diagrams in Series I to V somewhat easier, especially to those who are not familiar with the triangular diagram, a celluloid scale may be made with its divisions of the same spacing as on the diagrams. On this scale draw lines, along which the ratios of two components of the system are constant. These ratios are indicated in proportion of the *B* to the *A* component, so that the scale may be used on any diagram. It would be possible to draw these ratio lines on the diagrams but it would needlessly complicate them. When a person has gained a little experience in using the celluloid scale, he can then interpret the diagrams without its help. In other words, such a scale helps a beginner to see what the diagrams mean. Fig. 2 of the third paper shows such a celluloid scale.

The ratios are useful in this way: the silica and alumina enter the blast-furnace charge largely from the ore, and the ratio of silica to alumina in the slag is then mostly determined by the ore mixture. On the other hand, the ratio of lime to magnesia is controlled by the flux added to the charge and the relative quantities of lime and magnesia in the flux determine the lime-magnesia ratio.

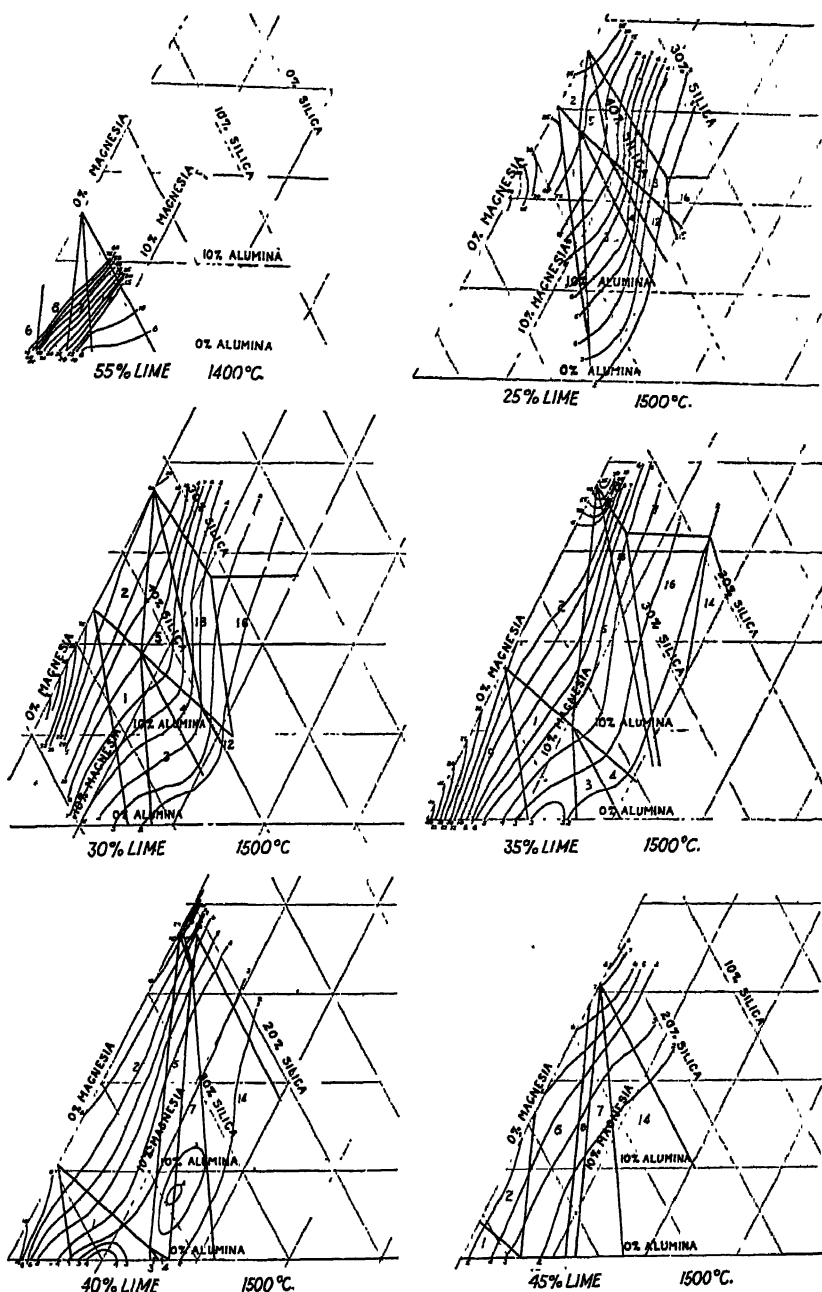
The use of the celluloid scale is illustrated in Fig. 3 of the third paper (p. 125). In that figure the scale is superimposed on Fig. 9, bringing the 20 per cent. line on the scale over the 20 per cent. silica line on the diagram and having the left side line of the triangle on the celluloid over the left-hand line (or 0 per cent. Al_2O_3) of the diagram. With the scale in this position, the ratio lines on it indicate the ratios of Al_2O_3 to SiO_2 in this particular diagram. Looking at the region between 35 and 50 per cent. CaO and from 5 to 25 per cent. Al_2O_3 , it will be seen that if the CaO is kept constant, the ratio of



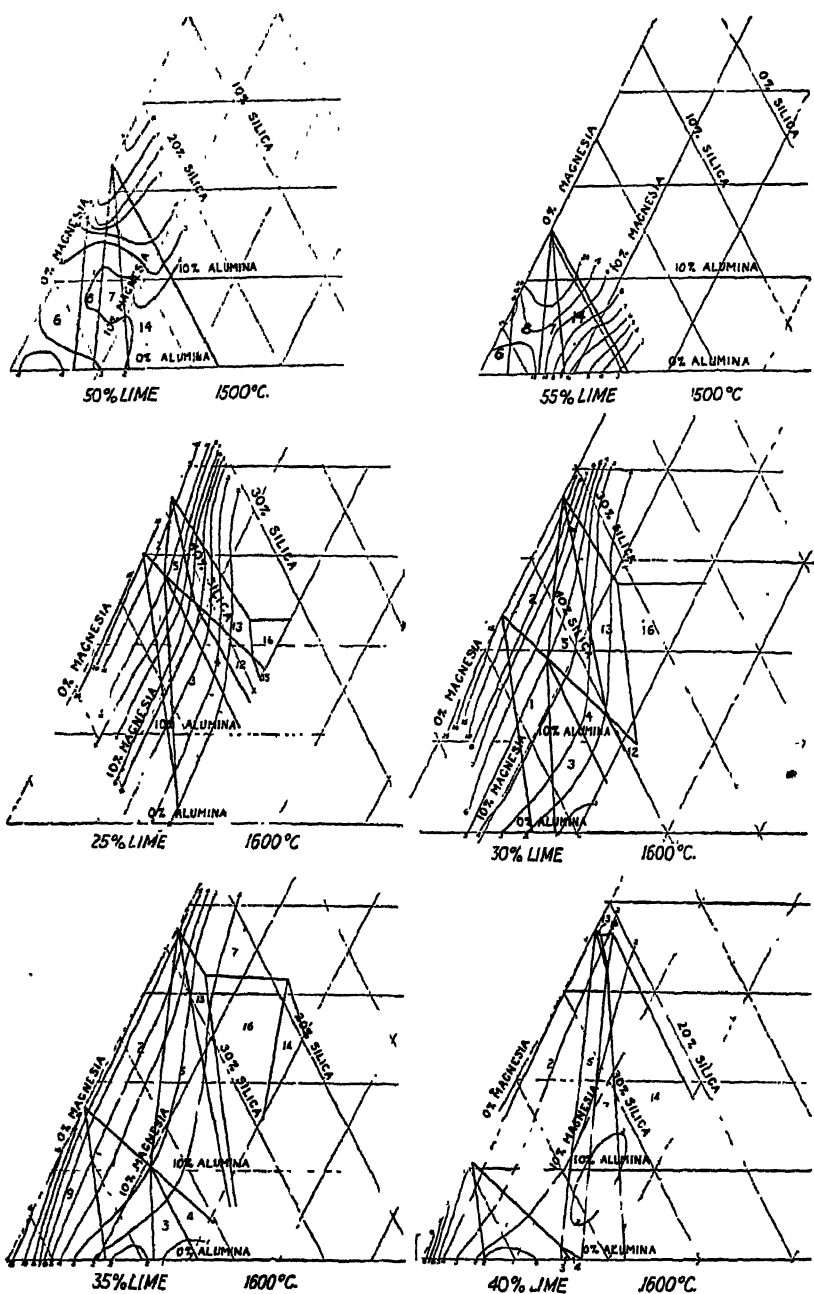
FIGS. 32-34.—VISCOSITY OF ALUMINA-LIME-MAGNESIA COMPOSITIONS, WITH SILICA VARYING 5 PER CENT.



FIGS. 35-40.—VISCOSITY OF SILICA-ALUMINA-MAGNESIA COMPOSITIONS, WITH LIME VARYING 5 PER CENT.



FIGS. 41-46.—VISCOSITY OF SILICA-ALUMINA-MAGNESIA COMPOSITIONS, WITH LIME VARYING 5 PER CENT.



FIGS. 47-52.—VISCOSITY OF SILICA-ALUMINA-MAGNESIA COMPOSITIONS, WITH LIME VARYING 5 PER CENT.

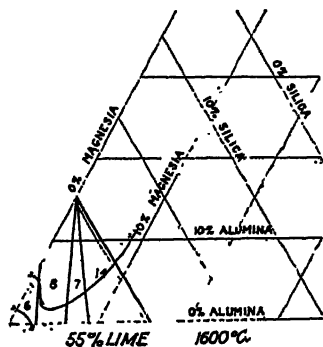
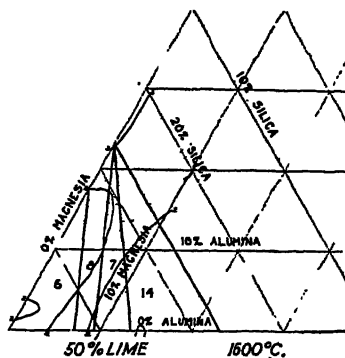
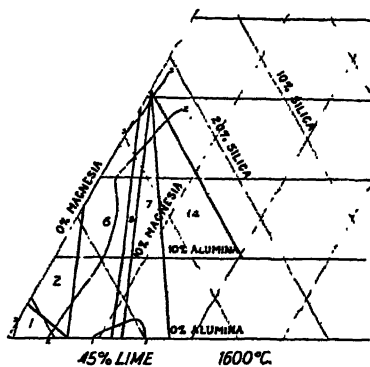
Al_2O_3 to SiO_2 may be changed over a considerable range without appreciably changing the viscosity. If the same procedure is followed with diagram 11, it will be observed that in this instance, too, there is relatively little change in viscosities when the Al_2O_3 : SiO_2 ratio is changed with constant CaO , as observed in the first example. From these diagrams it will be interesting to make some viscosity comparisons, as follows:

	Slag I	Slag II	Slag III	Slag IV
SiO_2 , per cent....	40	50	40	50
Al_2O_3 , per cent...	10	10	10	10
CaO , per cent....	50	40	40	30
MgO , per cent...	0	0	10	10
Viscosity (poises).	3	8	3	6

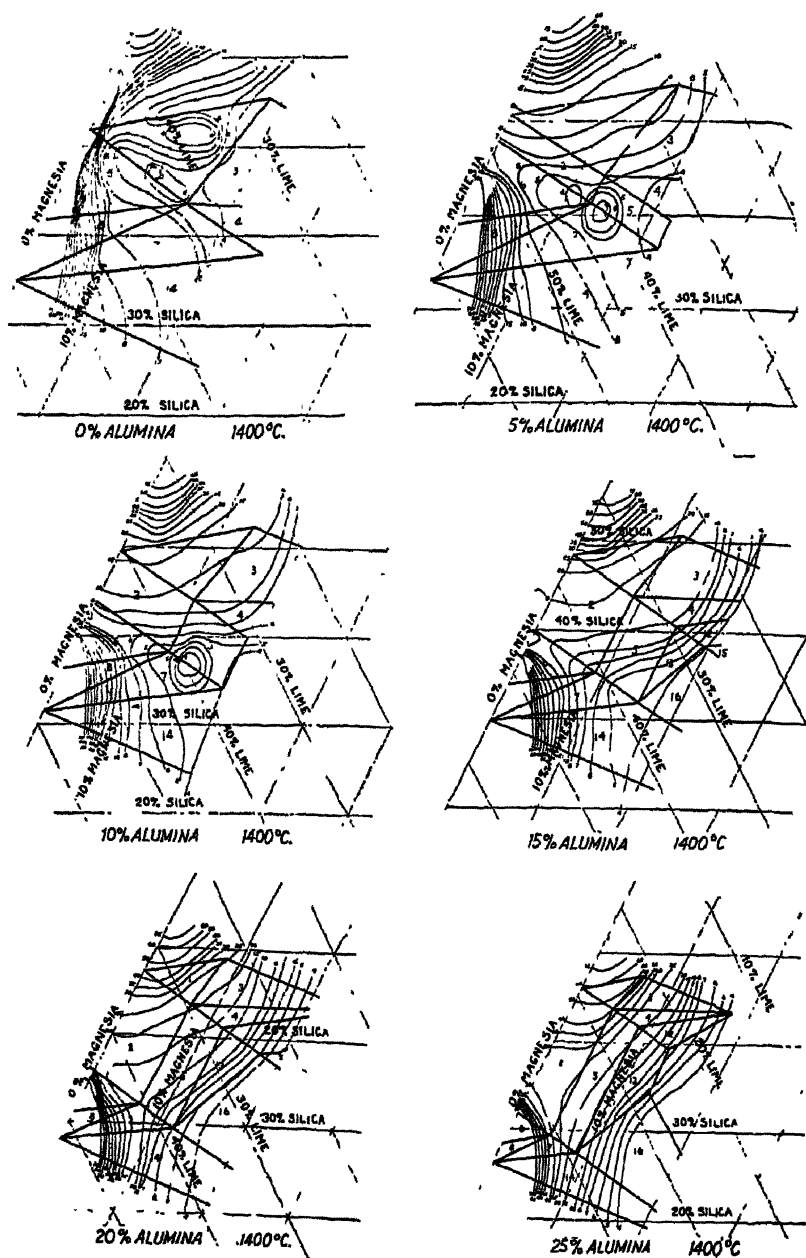
For any of the slags just compared it can be seen that if the lime and magnesia are kept constant, a considerable variation in the Al_2O_3 : SiO_2 ratio will only slightly affect the viscosity. In other words, the ore mixture may change considerably, but if the lime and magnesia are maintained constant, only slight changes in viscosity will result.

For another comparison, take diagram 64 of this report and superimpose the celluloid scale; the bottom line of the scale goes over the 20 per cent. SiO_2 line of the diagram and the left side line of the scale over the 0 per cent. MgO line of the diagram. Now examine the region between 42 and 50 per cent. CaO . Here the MgO : SiO_2 ratio does not affect the viscosity appreciably, whereas with higher or lower CaO content a change of this MgO : SiO_2 ratio has a decided effect on viscosity.

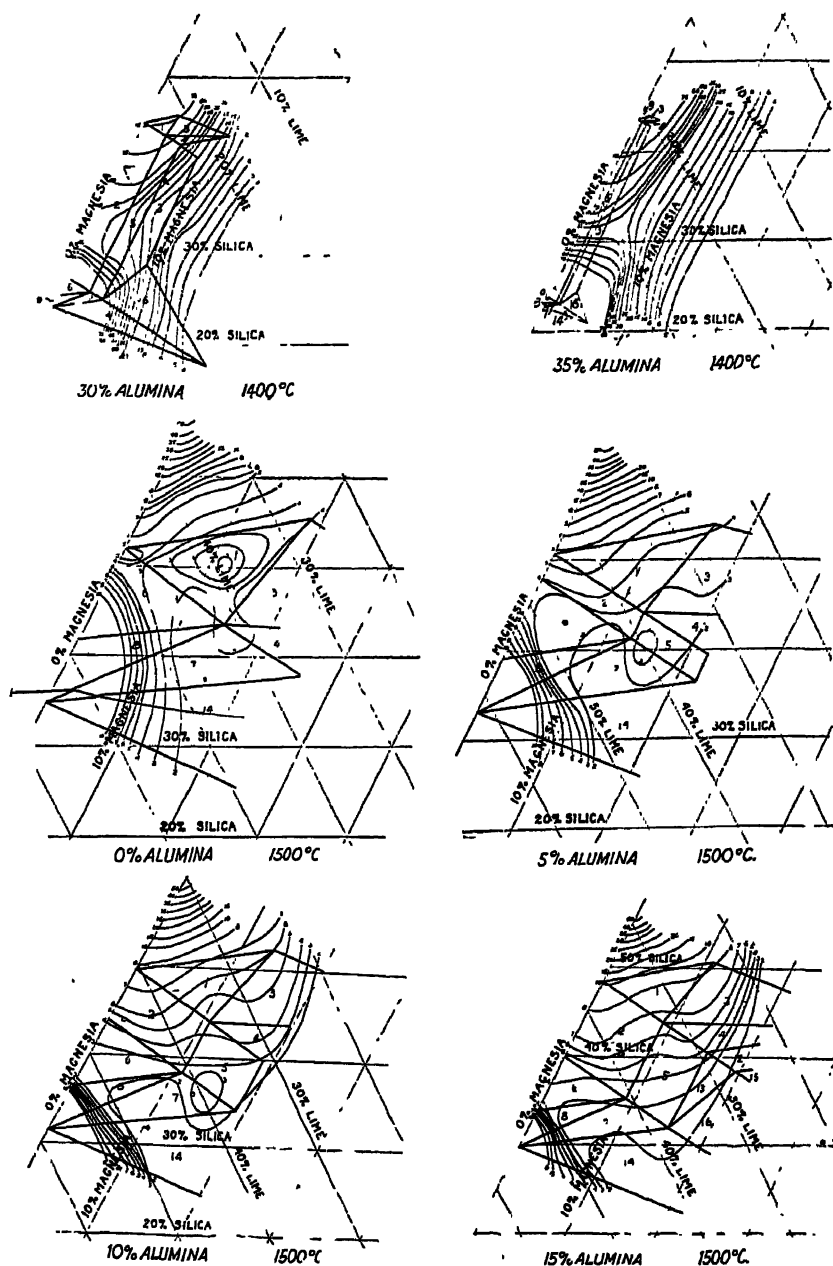
The effect of changes of temperature on the viscosity of any particular slag can be determined by reading the viscosity of the slag from a diagram



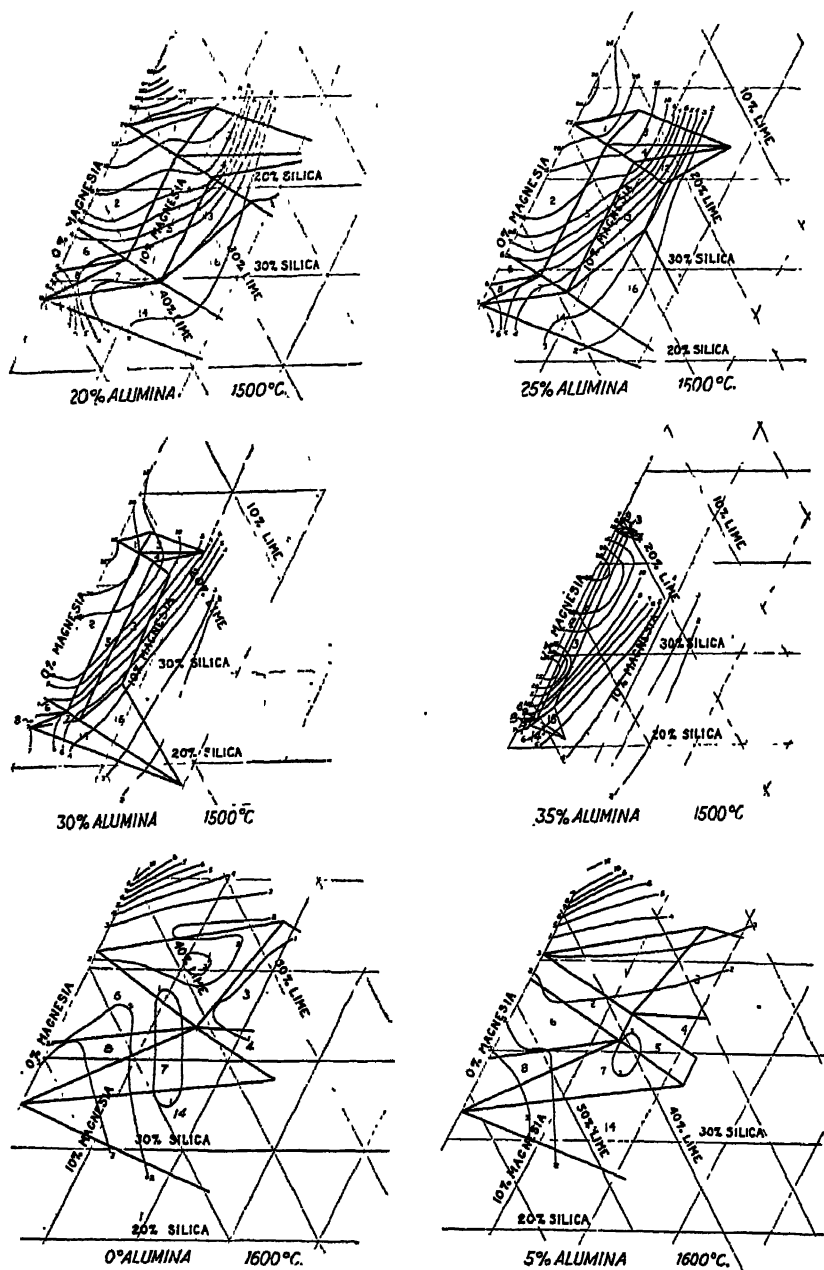
FIGS. 53-55.—VISCOSITY OF SILICA-ALUMINA-MAGNESIA COMPOSITIONS, WITH LIME VARYING 5 PER CENT.



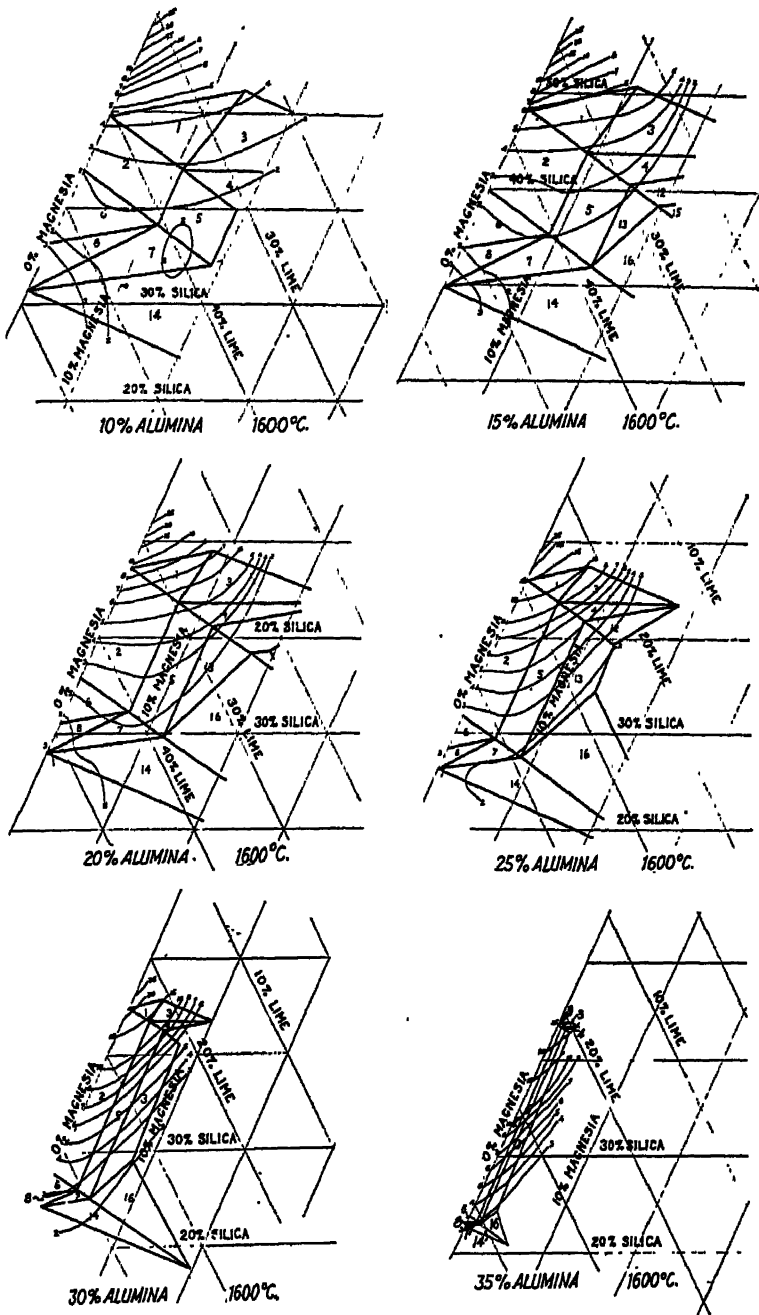
FIGS. 56-61.—VISCOSITY OF LIME-MAGNESIA-SILICA COMPOSITIONS, WITH ALUMINA VARYING 5 PER CENT.



FIGS. 62-67—VISCOSITY OF LIME-MAGNESIA-SILICA COMPOSITIONS, WITH ALUMINA VARYING 5 PER CENT.



FIGS. 68-73.—VISCOSITY OF LIME-MAGNESIA-SILICA COMPOSITIONS, WITH ALUMINA VARYING 5 PER CENT.



FIGS. 74-79.—VISCOSITY OF LIME-MAGNESIA-SILICA COMPOSITIONS, WITH ALUMINA VARYING 5 PER CENT.

at one temperature and comparing this reading with the same composition in the diagram at a higher or lower temperature. We have attempted to show this temperature variation in diagrams 19 to 23 of the third paper. By a study of these five diagrams a good idea of the temperature-viscosity variations may be obtained.

It should be borne in mind that the diagrams are all on the basis that the sum of the $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{CaO} + \text{MgO}$ is equal to 100 per cent., so that when blast-furnace slags are compared, the quantities of these constituents should be proportionally increased so that their sum will equal 100 per cent.

MATHEMATICAL AND GRAPHICAL DETAILS

Persons interested in the methods employed in reducing and studying the data of the experiments are referred to the second and third papers in this series. The diagrams of Series I to V are plane sections of equilateral tetrahedrons. This figure was chosen as being the most convenient for showing relations of four variables. Each slag composition studied was considered as made up of four substances, or minerals, together containing the chemical compounds alumina, lime, magnesia and silica, 100 per cent. value of each component being represented by an apex of the tetrahedron. Other substances, occurring in very small quantities in the slags, were disregarded.

The large Arabic numbers in the triangles of compositions on the diagrams which represent sections of a tetrahedron by the plane of the section are the numbers given to the tetrahedrons in the original publication² as follows:

Tetrahedrons (by Components)

No.

- 1 Akermanite, Anorthite, Calcium Bisilicate, Diopside.
- 2 Akermanite, Anorthite, Calcium Bisilicate, Gehlenite.
- 3 Akermanite, Anorthite, Diopside, Forsterite.
- 4 Akermanite, Anorthite, Forsterite, Monticellite.
- 5 Akermanite, Anorthite, Gehlenite, Monticellite.
- 6 Akermanite, Calcium Bisilicate, Gehlenite, Tricalcium Disilicate.
- 7 Akermanite, Calcium Orthosilicate, Gehlenite, Monticellite.
- 8 Akermanite, Calcium Orthosilicate, Gehlenite, Tricalcium Disilicate.
- 9 Anorthite, Calcium Bisilicate, Cristobalite, Diopside.
- 10 Anorthite, Clino-enstatite, Cristobalite, Diopside.
- 11 Anorthite, Clino-enstatite, Diopside, Forsterite.

² R. S. McCaffery and J. F. Oesterle: Constitution of Iron Blast-furnace Slags *Jnl. Iron and Steel Inst.* (1924) 111, 285.

Tetrahedrons (by Components).—(Continued)

- No.
- 12 Anorthite, Forsterite, Madisonite, Monticellite.
 - 13 Anorthite, Gehlenite, Madisonite, Monticellite.
 - 14 Calcium Orthosilicate, Gehlenite, Magnesite, Monticellite.
 - 15 Forsterite, Madisonite, Magnesite, Monticellite.
 - 16 Gehlenite, Madisonite, Magnesite, Monticellite.

WORK TO BE DONE

Several problems related to blast-furnace slags remain to be investigated and certain investigations begun should be completed. The work to be done may be itemized and outlined briefly as follows: (1) Electrical Conductivity, (2) Chemical Equilibrium, (3) Moisture, (4) Iron Oxides.

Electrical Conductivity.—A continuation of our study to determine the degree of dissociation in slags and the meaning of dissociation with respect to blast-furnace operating factors, such as sulfur solubility. The importance of continuing this work along these lines is due to the fact that we were the first observers who investigated electrical conductivity of slags. We did this in a collateral study developed during our viscosity work. It seems to afford a promising approach through its associated property, dissociation, to some of the complex problems of slags and may throw light on desulfurization.

Chemical Equilibrium.—A study of how far slags depart from equilibrium conditions as determined by petrological examination of chilled samples and the influence of this departure from equilibrium on a measurable physical property such as viscosity. It is not known exactly how far ordinary blast-furnace slags depart from equilibrium conditions and how such departure modifies their action.

Moisture.—The effect of moisture on the formation of slags and on their viscosity and other properties. It is known that moisture profoundly changes certain of the properties of slags, but there are no quantitative data available, and since the air blown into the furnace is continually varying in its moisture content, such data are important.

Iron and Manganese and Alkali Oxides in Slags.—The effect of iron, manganese and alkali oxides on viscosity, conductivity, etc. All blast-furnace slags contain oxides of iron, manganese and the alkalies, but their effect on blast-furnace slag properties is unknown quantitatively, but may be of great practical importance.

The results reasonably to be expected from these investigations would bring important benefits to blast-furnace owners and to the iron and steel industries in their several branches.

[For discussion, see page 135.]

Determination of Viscosity of Iron Blast-furnace Slags*

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(New York Meeting, February, 1931)

THIS paper is the report of an investigation to determine the relations between the viscosity, temperature and composition of that portion of the silica-alumina-lime-magnesia system⁽¹⁾ within which blast-furnace slags are found. The work reported in this paper was made possible by a grant of funds from Engineering Foundation. It is a part of a project, the determination of properties and structure of iron blast-furnace slags, upon which the laboratories of the University of Wisconsin have been at work for some years.

Three papers have been published, which have marked the progress of the study of iron blast-furnace slags at Wisconsin. The first,⁽²⁾ Desulfurizing Power of Iron Blast-furnace Slags, discussed the solubility of sulfur in slags that contained no magnesia and discussed the viscosity. The second,⁽³⁾ The Constitution of Iron Blast-furnace Slags, developed the constitutions of slags in the four-component system, silica-alumina-lime-magnesia, and pointed out an explanation of slag structure. Composition of Iron Blast-furnace Slags,⁽¹⁾ which was the third paper, gave a method of calculating the percentages of the various compounds present in slags when the amount of oxide was given and also an interpretation of quaternary equilibrium. Illustrations were given of the mineral composition of blast-furnace slags and some applications of composition results were shown.

Because of their relative ease of measurement, the viscosity-temperature relation for slags was selected as a factor which would be useful in correlating the physical properties of molten slags to furnace operation. With this in mind the viscosities of slags whose compositions are in that portion of the quaternary system, silica-alumina-lime-magnesia, in which blast-furnace slags occur, were thoroughly investigated.

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¹ Numbers in parentheses refer to the bibliography beginning on page 120.

The early literature on slag viscosity first brought out methods for the determination of fusibility or softening temperatures of slags, by means of deformation. Boudouard's⁽⁴⁾ study of the softening temperature of slags was based upon the principle of the Seger cone. Fulton⁽⁵⁾ employed the thermal method of the Geophysical Laboratory, to determine the melting points of a series of copper slags. By stirring the slag with a heavy platinum rod he obtained an approximation of the temperature at which the slag became fluid. In 1907, Goodwin and Mailey⁽⁶⁾ measured the viscosity of fused salts and mixtures up to 600° C. by a capillary flow process. Greiner⁽⁷⁾ observed the rate at which a platinum rod was withdrawn from molten sodium silicate (Na_2SiO_3) under the influence of a known constant force. Varying proportions of other substances were added and the relative viscosities were measured up to 1375° C. In 1908, Arndt⁽⁸⁾ used a modification of the Stokes method. He observed the rate of fall of an oblong platinum body through molten commercial glass of definite chemical composition. The apparatus was standardized with castor oil and results were obtained in poises at various temperatures. Staley⁽⁹⁾ in 1912 investigated the viscosities of certain borated glasses using a method similar to that employed by Arndt. A hollow platinum cylinder suspended in molten glass by a platinum wire was attached to the end of an arm of a balance. The rate at which the cylinder traveled through the melt was shown on a scale. Doelter's⁽¹⁰⁾ experiments with artificial diopside included the viscosity measurements of this compound in the molten state by timing the fall of a platinum sphere through the melt.

Until the investigation of Feild and Royster⁽¹¹⁾ on the viscosities of blast-furnace slags, no work on the particular silicates mentioned in this paper had been done. Their results covered a portion of the ternary system, silica-alumina-lime. The method they used was based on the principle of the Margules⁽¹²⁾ rotating cylinder. Since then a number of investigations have been made on the viscosity of glass. Williams and Cox⁽¹³⁾ have determined the variation of the viscosity of barium glasses with temperature by measuring at different temperatures the rate at which a platinum rod penetrated a mass of glass. By observing the rate of fall of a known weight attached to a carefully measured strip of glass which was fixed on one end, Twyman⁽¹⁴⁾ was able to measure the viscosity of glass at low temperatures. The determination of the actual mobilities of glasses of varying compositions near their annealing temperatures have been made by English.⁽¹⁵⁾ Washburn, Skelton and Libman⁽¹⁶⁾ have investigated the relations between viscosity, temperature and composition of lime-soda-silica melts within the field of common commercial glasses. Their apparatus was designed to use the principle of the Margules rotating cylinder and was capable of measuring viscosities within the range of 0.05 to 200,000 poises. Recently a number of investi-

gators have determined the viscosities of molten metals. Arpi⁽¹⁷⁾ used Poiseuille's method⁽¹⁸⁾ in obtaining the viscosities of cadmium, tin, lead, bismuth and the alloys lead-tin and lead-bismuth, from 550° C. to the melting point. Thielmann and Wimmer⁽¹⁹⁾ described an apparatus by which the viscosity of molten pig iron is determined by observing the amplitude of a system swinging in the molten metal. Losana⁽²⁰⁾ found that the Ostwald viscosimeter was impractical for fluid metals and alloys even below 400° C., and therefore constructed two special forms of apparatus. One consisted of two vertical bulbs connected at the bottom by a capillary U-tube, the other was a rotating viscosimeter for use at temperatures between 400° and 1000° C.

OBJECTS OF THIS INVESTIGATION

This investigation has five objects as listed below. This paper reports the work done under heading No 1.

1. To determine the relation between viscosity, temperature and composition of combinations of iron blast-furnace slag minerals which are part of the more extensive four-component system silica-alumina-lime-magnesia.

2. To correlate results of viscosity determinations with other physical properties of iron blast-furnace slag minerals as an aid in controlling furnace operation.

3. To determine mineral compositions which will give free-running slags suitable for iron blast-furnace operation.

4. To determine whether small changes of the oxide constituents may cause large changes in the physical properties.

5. To show the effect of magnesia upon the iron blast-furnace slag mixtures.

DESCRIPTION OF THE VISCOSITY APPARATUS

The apparatus used to determine the viscosities of silicates at high temperatures in this investigation is essentially similar to that described by A. L. Feild⁽¹¹⁾ in his paper on Method for Measuring the Viscosity of Blast-furnace Slag at High Temperatures. However, many important modifications were made in its construction (Fig. 1).

FIG. 1.—VISCOSITY APPARATUS.

- | | |
|---------------------------------------|--------------------------------------|
| a. Asbestos fiber packing | l. Suspension ribbon |
| b. Electrical terminals | m. Plane mirror |
| c. Water inlets | N. Brass stage for centering spindle |
| d. Water outlets | p. Weight |
| e. Leeds & Northrup optical pyrometer | r. Damping vanes |
| f. Scale | s. Castor-oil container |
| h. Nut for height variation | t. Furnace |
| i. Electrical insulation | v. Gear reducer |
| J. Water-cooled ball joint | w. Motor |
| K. Hollow steel shaft | |

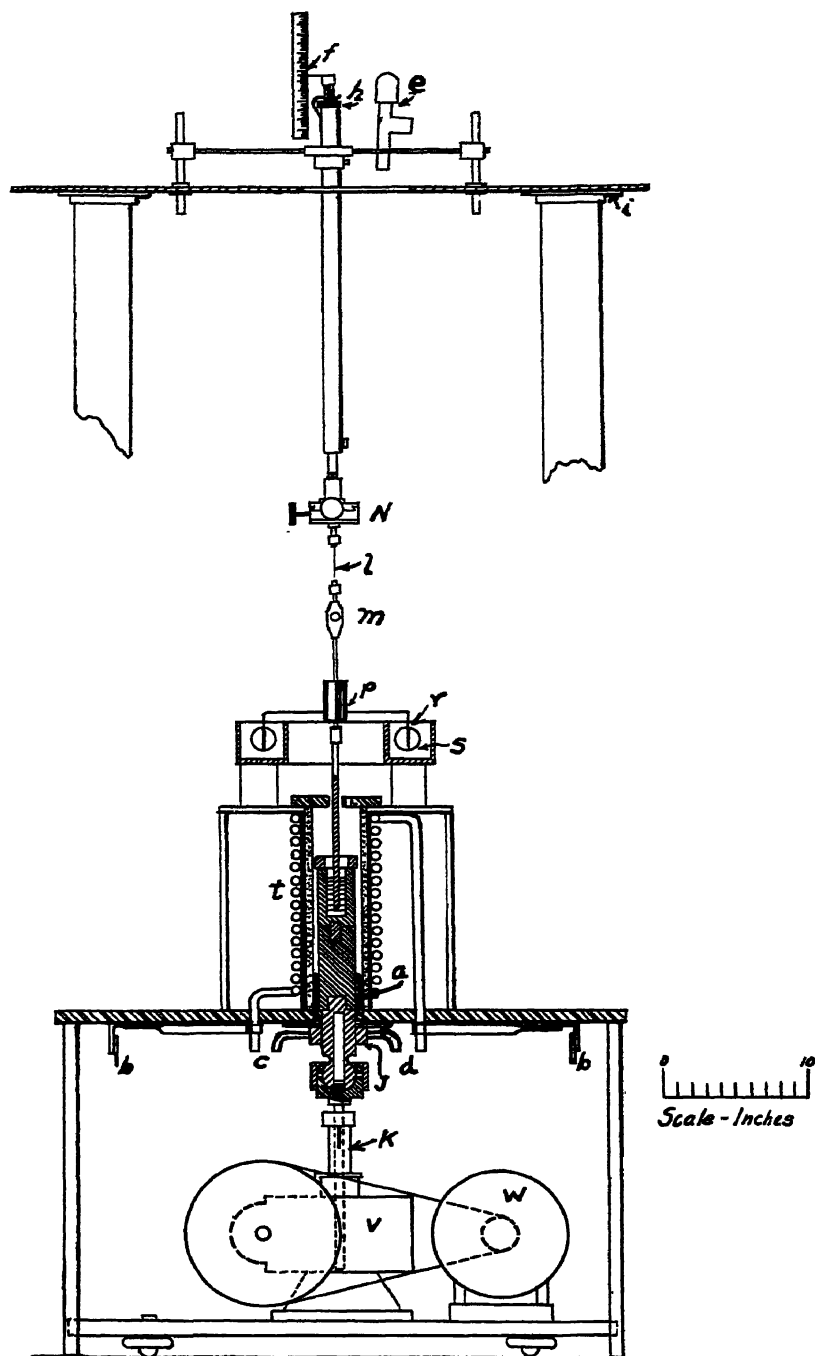
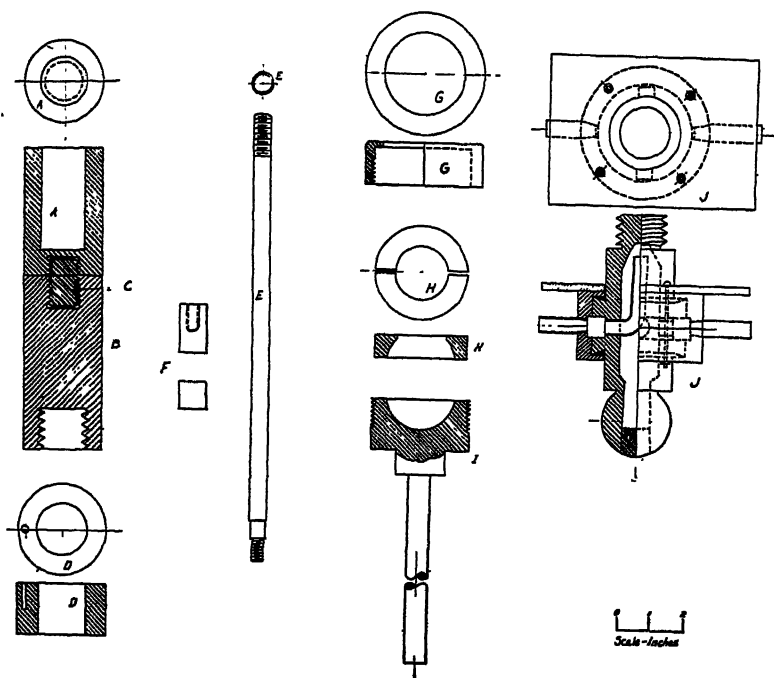


FIG. 1.—CAPTION ON OPPOSITE PAGE.

An Ajax-Northrup high-frequency induction-type furnace operated from a 35 kva. high-frequency converter supplies the necessary energy for heating. In this induction furnace, the secondary, in which the heating currents are set up, consists of a graphite crucible and its molten charge, while the primary consists of a tubular coil, $4\frac{1}{4}$ in. dia., of 28 turns and having suitable connections for water cooling. The coil is supported on a thick asbestos board and is completely enclosed in an asbestos board cylinder. An alundum tube which measures 4 in. outside diameter and 3



FIGS. 2 AND 3.—PARTS OF VISCOSITY APPARATUS

- | | |
|---------------------------------|--|
| A. Graphite crucible | F. Graphite spindle, immersed section |
| B. Graphite support | G. Steel nut |
| C. Graphite nipple | H. Split steel collar |
| D. Graphite ring | I. Steel socket |
| E. Graphite spindle, upper part | J. Ball joint and water cooling system |

in. inside diameter acts as a lining and is insulated from the coil by layers of mica. The desired control of furnace temperature is accomplished through the use of variable iron-cored series impedances connected in the primary circuit of the step-up transformer,⁽²¹⁾ and by inserting a variable air-cored inductance in series with the high-frequency circuit.

The high-frequency furnace has a number of advantages over the gran-annular type used by the U. S. Bureau of Mines. All the heat is confined within the furnace, heating is very rapid, the maximum furnace temperature obtainable is considerably above that necessary for the

investigation, temperature control is easily established, no gases are evolved in the furnace to interfere with temperature readings, furnace repairs are infrequent and one feels no discomfort in working close to it.

There is no movement of the slag by the high-frequency induction currents. Alternately applying and shutting off the furnace power gave identical viscosity readings for a given slag temperature.

The crucible and crucible support (*A* and *B*, Fig. 2) are accurately machined from Acheson graphite. It is necessary that they be interchangeable, since a crucible can be used for only one slag mixture. The crucible is $2\frac{3}{8}$ in. dia. and $3\frac{3}{4}$ in. long, while its bore is 3 in. in depth and $1\frac{5}{16}$ in. dia. A small graphite nipple (*C*, Fig. 2) joins the crucible to its support. The graphite ring *D* resting on the crucible increases its effective length and thereby helps to maintain a uniform temperature throughout the melt, while at the same time this ring lessens the amount of graphite necessary for each crucible. To prevent a rising column of gas from passing through the furnace while it is in operation, washed and dried asbestos fiber (Fig. 1 *a*) is gently packed around the lower end of the crucible support. This is an effective seal and very little oxidation of the crucible and its support occurs during a run. The furnace at all times is free from gases. The life of a crucible support is generally 40 to 50 hr. at high temperatures.

The crucible support is screwed on to a steel, water-cooled ball joint (*J*, Fig. 3), which consists of a hollowed steel cylinder with a thread on one end and a ball on the other. Two shoulders near its center support a movable box through which enters the chamber between the box and the steel cylinder. The water enters the cylinder either through a pipe bent upward or through a hole placed on the side opposite to the pipe inlet. Two fins at right angles to the inlet and outlet openings force the water along one of two paths, depending upon the position of the steel ball joint as it revolves. For one-half revolution the water is forced upward through the pipe against the inner wall of the threaded portion and is discharged through the hole opposite to the pipe inlet. During the second half of the revolution the water reverses its course, entering the hole and discharging through the pipe. This arrangement insures complete protection against overheating the steel threads. Asbestos packing and a heavy grease form a water-tight joint between the box and cylinder, yet allow the latter to turn easily while the former is stationary. An asbestos board fastened to the box with the four bolts that hold the halves together performs two functions; one, to act as an air seal at the bottom of the furnace, the other, to hold the box securely while the joint revolves.

The ball seats into a socket which is one end of a long spindle *I* (Fig. 3) while a split collar and nut *H* and *G* hold the joint in position. The spindle passes through a hollowed steel shaft *K* which is split for some distance from the top and which is keyed into a vertical gear reduction

(V, Fig. 1). A collar and set screw permit the halves to be drawn tightly against the spindle after it is set at the desired height. This allows the spindle to be raised or lowered within certain limits. The height of the crucible, its support and the ball and socket joint can be so adjusted that the asbestos board on the ball joint just touches the furnace bottom.

The vertical gear reduction type 5WV is manufactured by the Foote Brothers Gear and Machine Co. It has a speed reduction of 20:1. The reduction gear is belted to a $\frac{1}{3}$ -hp. class LK variable-speed alternating-

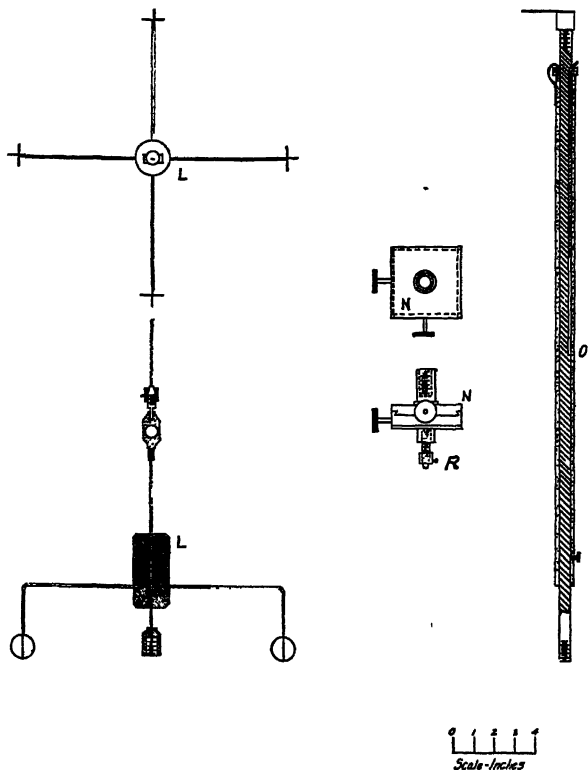


FIG. 4.—SUSPENSION SYSTEM.

L. Suspension system
N. Brass stage

O. Brass sleeve with steel rod
R. Chuck

current motor manufactured by the Kimble Electric Co. Its speed variation is from 500 to 2000 r.p.m. in either direction. The total reduction in speed, including gear reduction and pulley, is about 50:1, making it possible for the crucible speeds to vary between 10 and 40 r.p.m. The gear reduction and motor are mounted on a circular cast-iron plate. The plate can be leveled by three adjusting screws.

The suspension arrangement is supported from a triangular steel plate bolted to three 4-in. pipe posts, which in turn are securely bolted

to the concrete floor. The structure is rigid and is in no way affected by vibrations from moving parts.

The brass sleeve with its steel rod (*O*, Fig. 4) is held in a bushing rigidly attached to three horizontal rods. By means of a set screw the sleeve can be set at any height in this bushing. The steel rod passing through the sleeve can be lowered or raised a distance of 6 in. by means of a nut. To prevent turning of the rod, a key is set into the sleeve which slides in a keyway in the rod. The distance through which the rod or sleeve is moved can be accurately controlled by the pointer and scale.

The brass stage *N* (Fig. 4) is screwed to the bottom end of the steel rod. The former consists of three parts: The upper part which screws on to the rod is stationary; the central part can be moved horizontally in one direction through a distance of $1\frac{1}{2}$ in. and the lower part can be moved the same distance in a direction at right angles to the movement of the central part. The movable parts are independent of each other, thus permitting the locating of a small chuck *R* at any point lying in a square whose sides are $1\frac{1}{2}$ in. long. There is no play in any of the parts.

The steel suspension ribbon of hardened watch-spring steel chucked to the brass stage is 10 cm. in effective length, and suspends the remainder of the system *L* (Fig. 4). The suspension system consists of a frame which holds a $\frac{1}{2}$ -in. plane mirror, a central rod, a weight with four vanes, and a nut at the lower end of the rod. Bakelite is used for the mirror frame, as its low coefficient of heat conductivity protects the mirror from overheating. The mirror is so placed that its reflecting surface lies on the axis of the central rod. A weight of approximately 400 g. gives stability to the system when the graphite spindle is immersed in the melt. The weight may be moved along the central rod and can be secured at any point by means of a screw. Four cross vanes attached to the weight with steel rods dip into a circular trough filled with castor oil. The vanes serve to dampen any momentary disturbance which would keep the system constantly in vibration. A graphite spindle (Fig. 2, *E*, *F*) is screwed into the nut at the lower end of the central rod. This spindle is of two parts. The upper part *E*, which extends out of the furnace, is $\frac{5}{8}$ in. dia. One end is threaded to enter the nut on the suspension member. The other end is turned to $\frac{3}{8}$ in. and has a short $\frac{5}{16}$ -in. threaded portion which screws into the square graphite end² *F*.

² The question regarding the use of a *square graphite spindle* for slag viscosity measurements and the reason why other materials were not substituted in its stead may be answered through discussing the requirements of a material for this purpose.

The use of the square spindle was a direct outgrowth of an extensive but very unsatisfactory test with a cylindrical spindle of $\frac{1}{2}$ in. dia. The unsatisfactory operation of the cylindrical spindle was ascribed to a number of causes, chief among them being: (1) most slags do not wet graphite; (2), there was evidence of slip between the partly solidified slag and the spindle, and (3), for this size of spindle the torque

The square end is $1\frac{1}{4}$ in. long, 1 in. across opposite angles of the square and approximately $\frac{3}{4}$ in. between the flat surfaces. It is this section of the spindle that is immersed in the slag. The center lines of the graphite spindle, the central rod, the plane mirror and the suspension ribbon form a straight line.

A light source at a distance of 2 m. from the apparatus projects a beam of light on the mirror from which the image of the light filament is reflected back upon a straight 2-m. scale placed exactly 2 m. away. The light source is just above the center of the 2-m. scale and for the initial reading during slag viscosity determinations the reflected image falls on the center of the scale. The scale is at right angles to the reflected beam. This arrangement permits viscosity determinations with the crucible revolving in either direction.

for very fluid slags was small and could not be measured with the degree of accuracy desired.

The apparatus for measuring viscosity of slags was calibrated with castor oil, a substance that wets graphite. Its viscosity at various temperatures was known. On replacing the oil with molten slag, conditions of operation are somewhat different in that the slag wets neither crucible nor spindle. An opportunity for slippage between the spindle surface and slag presents itself and does occur. In some instances the spindle could be easily turned in the melt after it had almost solidified. A true measure of viscosity requires that slippage shall occur between adjacent layers of slag only. As pointed out, these requirements are not always fulfilled when using cylindrical spindles in the viscosity apparatus.

To measure the viscosity of fluid slags with the cylindrical spindle, a sensitive suspension ribbon was necessary to give a deflection sufficient to be detected. Because of the inertia of the suspension system a slight deflection or twist in a ribbon of this size will not return the system to a zero position. It is, therefore, with difficulty that the initial or zero for the instrument is obtained.

The use of the square spindle removed most of the objections inherent in the cylindrical spindle. As the crucible revolves the slag is forced to pass around the corners of the spindle; each corner with the crucible inner wall forms an orifice through which the slag must flow. The speed of the crucible is never so great as to cause turbulence in the slag, and under the condition of straight-line motion the force acting on the spindle through the flow of slag around the corners is directly proportional to the slag viscosity. Not only then is the total force which deflects the spindle dependent upon the drag resulting from the friction between the slag layers, but it is also determined by the force acting on the spindle through the flow of slag around its corners. As a consequence of the latter force a stiff suspension ribbon is necessary even for the most fluid slags, there is a greater stability in operation of the apparatus and there is greater accuracy in the measurements of slag viscosity.

When the conditions of slag viscosity measurements are considered, it becomes difficult to select materials other than graphite for the crucible and spindle material. Slags are corrosive and will attack the oxide refractories, zirconium oxide excepted, that are in common use. At a temperature of 1700°C. , to which a number of slags were heated, such refractory materials are weak and fragile, and the action of the slag on them is rapid with a consequent change in slag composition. On the other hand, graphite is highly refractory, it is strong at high temperatures, and it is not corroded by slag. The one objection to graphite, its inability to be wetted by slag, is removed by the use of the square spindle.

The complete apparatus is shown in Fig. 5; the suspension element, spindle and furnace are illustrated in larger scale in Fig. 6.



FIG. 5.—COMPLETE VISCOSITY APPARATUS.

SPINDLE DESIGN

The selection of the spindle design employed in this work followed after considerable preliminary work with various spindle shapes. In the first experiments a $\frac{1}{2}$ -in. cylindrical spindle was tried. It was observed that the torque developed on this spindle in fluid slags was very small and difficult to measure. The use of a sensitive suspension ribbon did not alleviate this difficulty but rather accentuated the errors in viscosity

measurements. Some of the difficulties encountered with the sensitive ribbon were the uncertainty of correct initial reading and the fluctuations in spindle deflection. The slightly twisted ribbon would not bring the suspension system to a constant reading when the crucible was stationary, because the small torque developed in the ribbon could not overcome

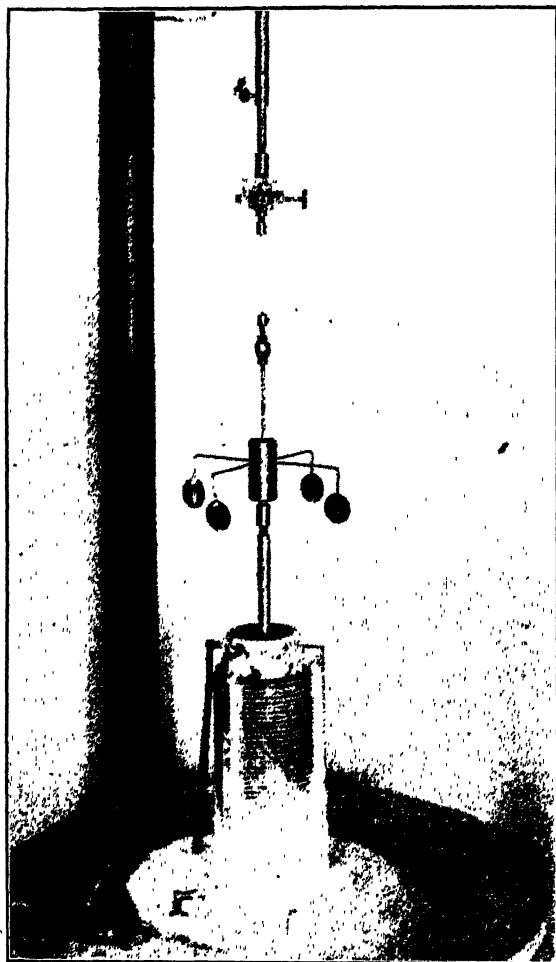


FIG. 6.—SUSPENSION ELEMENT, SPINDLE AND FURNACE.

the inertia of the system. High speeds were required to obtain readable deflections for fluid slags. At high speeds, however, the spindle would not stay in the center of the crucible; instead it tended to be thrown to the side of the crucible. Spindle deflections were increased by the presence of slight amounts of froth or foam on the surface of the molten slag. The froth, because of its adherence to the spindle surface, increased the

deflection when viscosity measurements were made. In some instances considerable deflections were caused by movements of heated air about the suspension system.

Surface tension of slags enters into the problem of slag viscosity measurements. Its effect would vanish if the diameter of the spindle at the slag surface became vanishingly small, but such small diameters at this point are not practical. For small cylindrical spindles the surface tension had a noticeable effect upon slag viscosity measurements.

Another factor is of importance in slag viscosity determinations. The majority of slags at temperatures at which their viscosities were determined do not wet graphite. Instead of measuring the slip between concentric cylinders of slag, a true measure of viscosity, the slip may occur between the two dissimilar materials, graphite and slag. Unless the frictional force between the graphite and slag is greater than the frictional force between layers of slag, the spindle deflection will not be a true measure of viscosity. A number of instances were noted in which the cylindrical spindle remained stationary in the rotating crucible after the

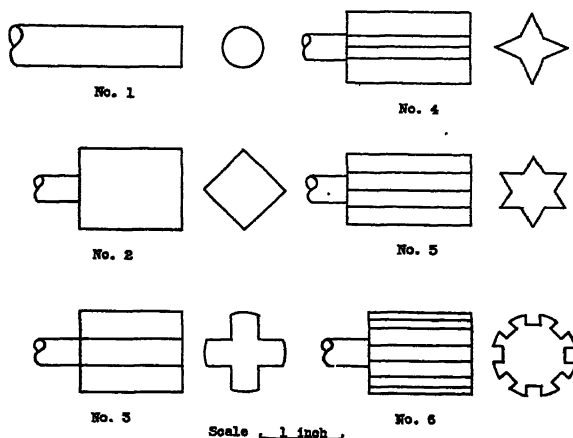


FIG. 7.—EXPERIMENTAL SPINDLE DESIGNS.

slag apparently had solidified. Since the accuracy of viscosity determinations of fluid slags was uncertain with its use, the cylindrical spindle was not employed in this investigation.

A number of spindles were designed to lessen the effect of surface tension, to increase the drag of fluid slags and to remove the possibility of slip between graphite and slag. By lengthening and increasing the diameter of the submerged portion of the spindle and by keeping the spindle at the slag surface as small as practicable, the relative effect of surface tension was minimized. Larger spindles required a heavier suspension ribbon even in the most fluid slags. Cylindrical spindles of various diameters and lengths were fluted longitudinally in an attempt

VISCOSITY OF IRON BLAST-FURNACE SLAGS

to entrap slag around the spindle. Such spindles would correspond roughly to spindles of slag of definite size and all slip would occur between slag layers. Star-shaped spindles of four or more points and the square

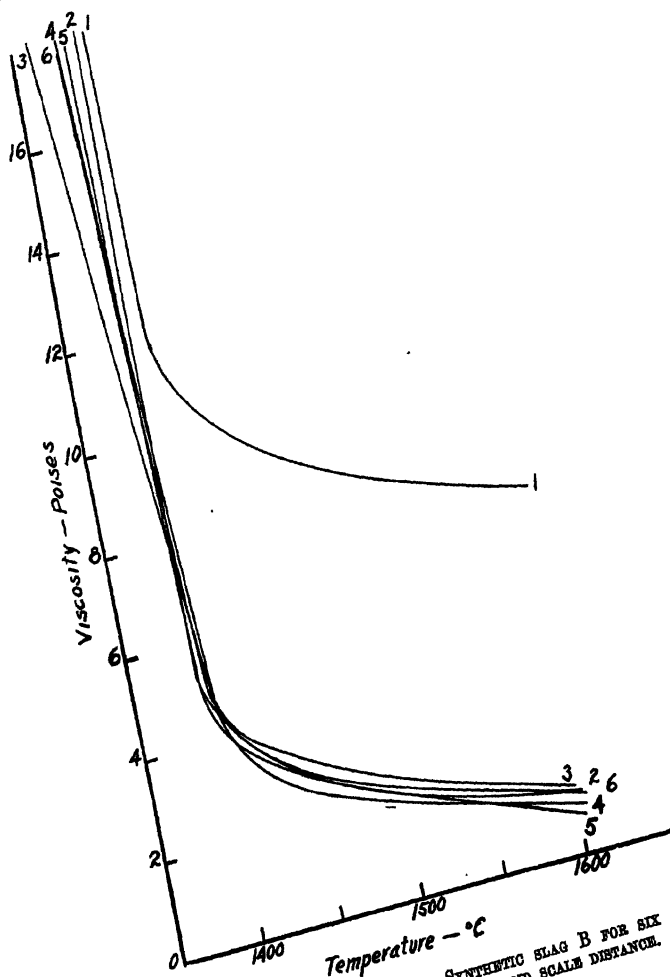


FIG. 8.—VISCOSITY-TEMPERATURE CURVES. SYNTHETIC SLAG B FOR SIX SPINDLE DESIGNS, USING SAME SUSPENSION, SPEED AND SCALE DISTANCE.

spindle, ultimately adopted for the investigations, were tried. Some of these experimental spindles are illustrated in Fig. 7. Viscosity measurements with the various spindles of the latter designs were in excellent

agreement with each other. Fig. 8 shows the viscosities determined with one of our synthetic slags using a round spindle, compared with the results with other spindles of the designs shown in Fig. 7. The spindle of square cross-section was selected because of its ruggedness and ease of machining.

TEMPERATURE MEASUREMENTS

The temperatures of the silicates were measured with a Leeds & Northrup two-range optical pyrometer. This was mounted on the triangular plate above the furnace, and was sighted on the slag through a small opening in an asbestos board which covered the furnace tube. As the condition in the furnace was not that of a black body, it was necessary to calibrate the optical pyrometer against a standard platinum-platinum rhodium thermocouple. A $\frac{1}{2}$ -in. graphite rod bored and lined with a silica tube served as a protection tube for the thermocouple. It was inserted in the center of the crucible of molten slag and simultaneous readings were taken with the optical pyrometer and the thermocouple. Two thermocouples were used in this work; one was calibrated by the U. S. Bureau of Standards, the other by Prof. C. E. Mendenhall, of the Physics Department of the University of Wisconsin. Temperatures between 1000° and 1550° C. were obtained in this manner. For higher temperature values, it was necessary to extend the temperature-milliamperage curve beyond the measured points. The temperature correction was equivalent to that for a material whose emissivity is 0.65.

SLAG MATERIALS

The mineral compounds were made from pure oxides of lime, magnesia, alumina and silica. Charges of 2000 g. were melted at one time in a graphite crucible by means of a high-frequency induction furnace. After each melt the slag was ground, sampled and analyzed to determine the percentage of each constituent oxide. Each compound was fused and analyzed four times to obtain a homogeneous mixture and to correct by any additions that were necessary. The final analysis corresponded with the percentage composition of the minerals and combinations as given in Table 1.

The minerals and mineral combinations of Table 1 were used in forming binary, ternary and quaternary mixtures of slag minerals. In proportioning the mixtures of these mineral compounds, each mineral constituent was accurately weighed and the entire charge thoroughly mixed before the melt was put into the crucible. Analyses of two mixtures chosen at random, after completing the viscosity and conductivity determinations, were as shown in Table 2. Since the percentages of the oxides analytically determined were in good agreement with the calculated

compositions, the mineral compositions of the slags were obtained by weight proportioning only.

TABLE 1.—*Composition of Minerals and Combinations*

Mineral	Chemical Formula	CaO, Per Cent.	MgO, Per Cent.	Al ₂ O ₃ , Per Cent.	SiO ₂ , Per Cent.
Akermanite.....	2CaO.MgO.2SiO ₂	41.14	14.79		44.07
Anorthite.....	CaO.Al ₂ O ₃ .2SiO ₂	20.16		36.65	43.19
Calcium bisilicate.....	CaO.SiO ₂	48.28			51.72
Diopside.....	CaO.MgO.2SiO ₂	25.90	18.62		55.48
Gehlenite.....	2CaO.Al ₂ O ₃ .SiO ₂	40.91		37.18	21.91
Madisonite.....	2CaO.2MgO.Al ₂ O ₃ .3SiO ₂	23.62	16.98	21.46	37.94
Monticellite.....	CaO.MgO.SiO ₂	35.84	25.77		38.39
Tricalcium disilicate, 75.25 %; calcium bisilicate, 24.75.....		55.85			44.15
Calcium bisilicate, 74.98 %; cristobalite, 25.02.....		36.20			63.80
Calcium orthosilicate, 55.00 %; gehlenite, 33.07; tricalcium disilicate, 11.93.....		56.30		12.30	31.40
Calcium bisilicate, 13.57 %; gehlenite, 43.25; tricalcium disilicate, 43.18.....		49.44		16.08	34.48

OPERATION OF THE VISCOSITY APPARATUS

In assembling the apparatus for the determination of viscosities of molten silicates, it is necessary that the crucible revolve about its central axis and that the spindle enter the slag centrally with respect to the crucible walls. The first requirement is met by means of the ball and socket joint to which the crucible support is attached. With careful adjustment the crucible is clamped in a truly vertical position. Once set, there is no danger that the alignment will be disturbed. To fulfill the second requirement the adjusting arrangement to which the suspension ribbon and system is held serves remarkably well. The centering is accomplished through observing the position of the spindle in the molten slag. If there is any eccentricity it can be detected through the behavior of the apparatus while in operation.

Approximately 135 g. of the pulverized slag is placed in the crucible. As the crucible does not hold the entire charge in the pulverized state a portion must be added after the first is melted. When the charge is completely melted, it is thoroughly mixed with a graphite stirring rod in order that the melt shall be homogeneous and free from bubbles. A

small amount is withdrawn on the end of a cool graphite rod and is used later to raise the slag to its proper height. The graphite spindle is lowered to the bottom of the crucible, then carefully raised to a position $1\frac{3}{4}$ in. above the bottom. Small bits of the slag, previously withdrawn, are added to the melt until the slag in the crucible just reaches to the bottom of the spindle. Thus each charge has a known volume in its molten state. However, this does not take into account volume changes with

TABLE 2.—*Analyses of Mixtures*

Mixture	Minerals	Mineral Composition, Wt. Per Cent.	Oxide Composition		
			Oxides	Calculated from Mixtures, Per Cent.	Determined by Analyses, Per Cent.
I	Akermanite.....	60	CaO	41.05	41.53
	Gehlenite.....	40	MgO	8.87	8.02
			Al ₂ O ₃	14.87	15.25
			SiO ₂	35.21	35.16
II	Gehlenite.....	30	CaO	46.07	46.57
	Calcium bisilicate.....	70	Al ₂ O ₃	11.15	11.98
			SiO ₂	42.78	42.43

the temperature, but they are small and can be neglected in this work. After the height of the slag has been established, the spindle is again lowered until it is $\frac{3}{4}$ in. above the crucible bottom. The square end of the spindle will then be completely submerged in the molten slag.

Centering of the spindle is done while the damping vanes are raised above the castor oil. This is accomplished with the aid of the brass stage. In the beginning, the image of the lamp filament is brought to the center of the 2-m. scale by adjusting the position of the upper chuck which supports the suspension system. The spindle is then moved in the crucible by means of the brass stage until it appears, by visual inspection, to be in center. The upper chuck is again adjusted to bring the image of the lamp filament to the center of the scale. Adjustments in centering of spindle and light are continued until there is no noticeable displacement. The damping vanes are then lowered into the circular trough of castor oil and the spindle is tested for eccentricity. This eccentricity test is made by noting the initial reading of the light beam before the vanes are lowered into the castor oil and while the crucible is stationary, then determining the light-beam reading by recording the deflection of the beam after the vanes are lowered and when the crucible is rotated at a definite rate in the two directions while the temperature of the slag is constant. If this reading does not coincide with the one recorded before the vanes are lowered, the spindle is not in the center of the crucible.

Previous experiments on various heavy oils have shown that the spindle tends to center itself if the velocity of the crucible does not surpass a critical value. Although our tests further showed that the actual deflection of the light beam was not altered by a slight eccentricity, our tests did show that the initial reading, as determined by revolving the crucible at the same speed in the two directions, is affected by eccentricity.

The path described by the light beam is a further aid in centering the spindle. If it does not follow a horizontal plane it is necessary to move the spindle in a direction at right angles to the light beam until the path of the reflected beam falls on a horizontal plane. This adjustment, together with the establishing of the initial light readings, gives a very direct means for centering the spindle, which we believe we are the first to apply.

It is very important that the initial reading be taken, because it is the difference between the initial reading and the deflected readings that determines the angles of deflection. If the former is wrong, the measured differences have a fictitious value.

If care is exercised, the spindle can be used for about three heats, or an actual time in the furnace of 6 hr. The part that is submerged in the slag is entirely unaffected by it. Spindles measured before and after use showed little or no loss in size, except that portion above the melt, which slowly oxidizes. To seal the furnace as well as possible, asbestos fiber is loosely packed between the crucible support and furnace wall, thereby sealing the bottom of the furnace against rising columns of air. The top of the furnace is covered with asbestos board, which is split through the center and contains an opening for the spindle and one through which to sight an optical pyrometer on the melt. Even with this precaution, the spindle will neck at the point where it passes through the asbestos board.

The crucible is generally revolved at a speed of 20 r.p.m. For most slags this speed gives a large deflection. With speeds approaching 60 r.p.m., the system is no longer stable, for the spindle is thrown outward against the side of the crucible. Actual tests with slags and oils have proved that the twist in the suspension ribbon is proportional to the speed of the crucible, at least within the ranges of the apparatus. As an example of this proportionality, the results on one blast-furnace slag are given in Table 3. In this test the temperature of the slag was maintained constant at 1440° C.

Before the viscosity of the slag is determined, it is necessary to keep the slag molten for some time. Viscosity measurements taken immediately after the slag is molten are very erratic and cannot be duplicated by other trials. In some cases an hour is required to obtain constant readings. The probable cause of this phenomenon is the result of slow diffusion and solution of the slag minerals in each other. No slag vis-

TABLE 3.—*Results of Test of One Slag*

Slag Analysis		Crucible Speed, R.P.M.	Actual Deflection, Cm.	Angle ϕ , Deg.	$\frac{\phi}{S}$	Viscosity in Poises
Oxides	Calculated on Basis of 100 Per Cent.					
CaO.....	37.91	9.50	3.3	0.94	0.0989	3.310
MgO.....	18.42	15.25	5.3	1.51	0.0990	3.312
Al ₂ O ₃	7.44	20.30	7.4	2.12	0.1045	3.495
SiO ₂	36.23	24.25	8.4	2.41	0.0995	3.325
		28.50	10.2	2.92	0.1026	3.430

cosities are measured until there is no variation in viscosity at a given temperature.

When the temperature of the slag is at the maximum value to which it is to be heated, the crucible is kept revolving and readings are simultaneously taken of the light-beam deflection, the crucible speed and the temperature of the melt. The temperature of the melt is slowly dropped at a rate of about 5° C. per minute, and as it falls the light deflection, the crucible speed and the temperature are read at short intervals. The speed is instantaneously measured with a tachometer that has been calibrated against a revolution counter.

These data are used in computing the absolute viscosity of the slags. As the light scale is at right angles to a line drawn from the source of light to the mirror, and is at a distance of 2 m. from the mirror, the actual deflection divided by 200 will give the tangent of an angle that is equal to the sum of the angles of incidence and reflection.

If ϕ = the total angle in degrees

a = actual deflection in centimeters

b = perpendicular distance of mirror from scale in centimeters

S = speed of crucible in revolutions per minute

K = constant for the steel ribbon

η = viscosity in absolute units (poise).^{*}

$$\text{Then} \quad \phi = \tan^{-1} \frac{a}{b}$$

$$\text{and} \quad \eta \text{ (Poises)} = \frac{K\phi}{S}$$

This expression permits the calculation of the viscosity when the actual deflection, the speed of the crucible and the constant for the ribbon are known. Constant K was determined by calibrating the ribbon against castor oil whose viscosity at 20°, 23°, and 26° C. was determined by the U. S. Bureau of Standards. Since η is known and ϕ and S are

^{*} A poise is a unit 100 times greater than the viscosity of water at 20° C. The viscosity of the castor oil at the same temperature is 10.2 poises.

determined, K can be calculated. The constant for the suspension ribbon used is 33.44. Since the length of the suspension ribbon between the chucks is always 10 cm., K will remain constant for the wire. A second calibration after a month's use gave identical values for K . A typical data sheet illustrating the method of viscosity measurement is shown in Table 4.

COMPARATIVE TESTS

To determine the nature of the flow we were observing, a series of tests was made in which the deflection angle and the speed were observed. If

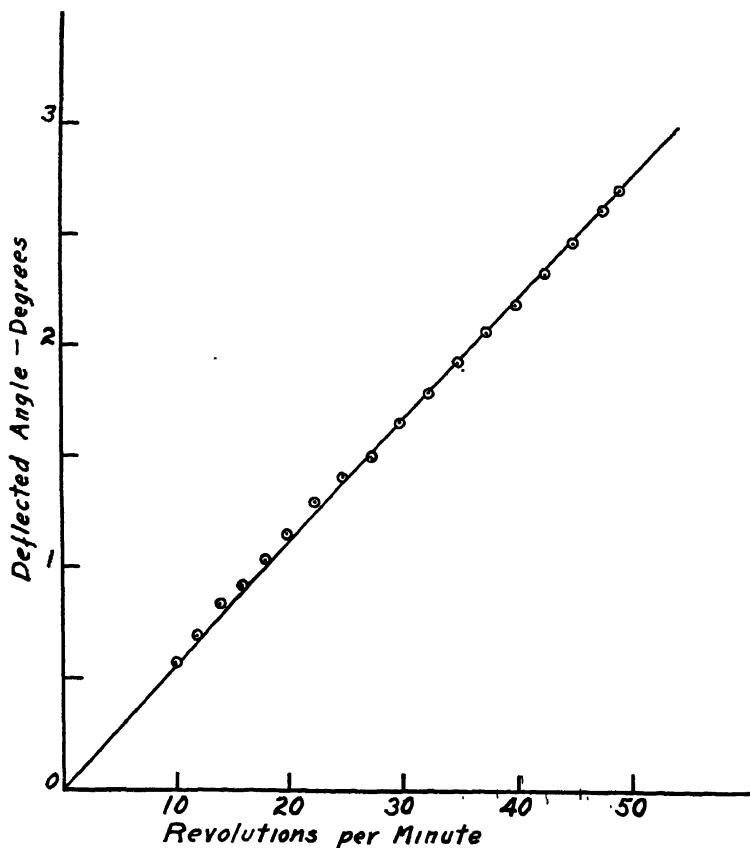


FIG. 9.—DEFLECTED ANGLE-CRUCIBLE SPEED. U. W. CASTOR OIL; $\frac{1}{2}$ -IN. ROUND SPINDLE. 22.5° C.

it were viscous flow with straight-line movement of the particles, then the deflection-speed graph would be a straight line passing through the origin. These graphs for castor oil employing a $\frac{1}{2}$ -in. round, a 1-in. round, and a square spindle 1 in. on the diagonal are shown in Figs. 9, 10 and 11. In all of our viscosity work we never exceeded a speed of

25 r.p.m., which is well below the speed range shown in Figs. 9, 10 and 11, all of which show that there was no turbulence because the curve is a straight line passing through the origin.

Figs. 9 and 10, which employed a $\frac{1}{2}$ -in. and a 1-in. round spindle in a crucible of the standard diameter which we always employed, in each of

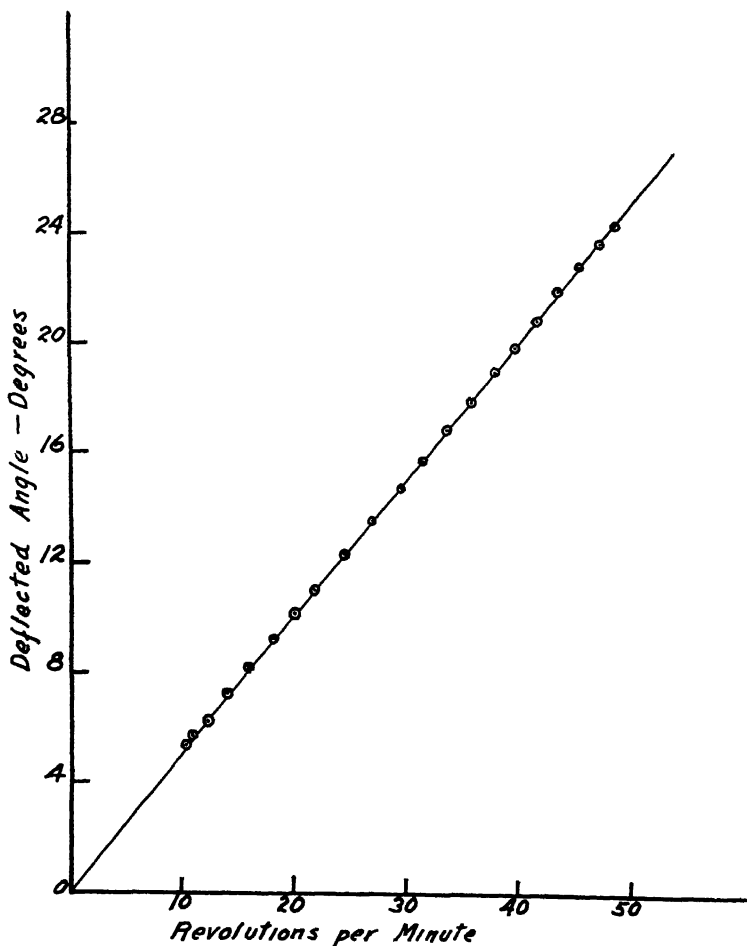


FIG. 10.—DEFLECTED ANGLE—CRUCIBLE SPEED. U. W. STANDARD CASTOR OIL; 1-IN. ROUND SPINDLE. 17° C.

the above cases, show that viscosity measurements in our type apparatus within the limits of dimension indicated above give the same results. In other words, the ratio of spindle diameter to crucible diameter within the range employed by us does not affect the viscosity measurement.

Herty used a formula for viscosity similar to that above⁽²⁷⁾ and he illustrates graphically (p. 7 of the paper cited) his calibration curve for

castor oil. Herty's graph approaches a parabola whereas obviously it should have been a straight line. On this basis he makes a comparison (pp. 18-19) between his determination of viscosity on one of our slags and our result on the same slag, made some time ago. To clear up this difference between us, three synthetic slags were made in our laboratory

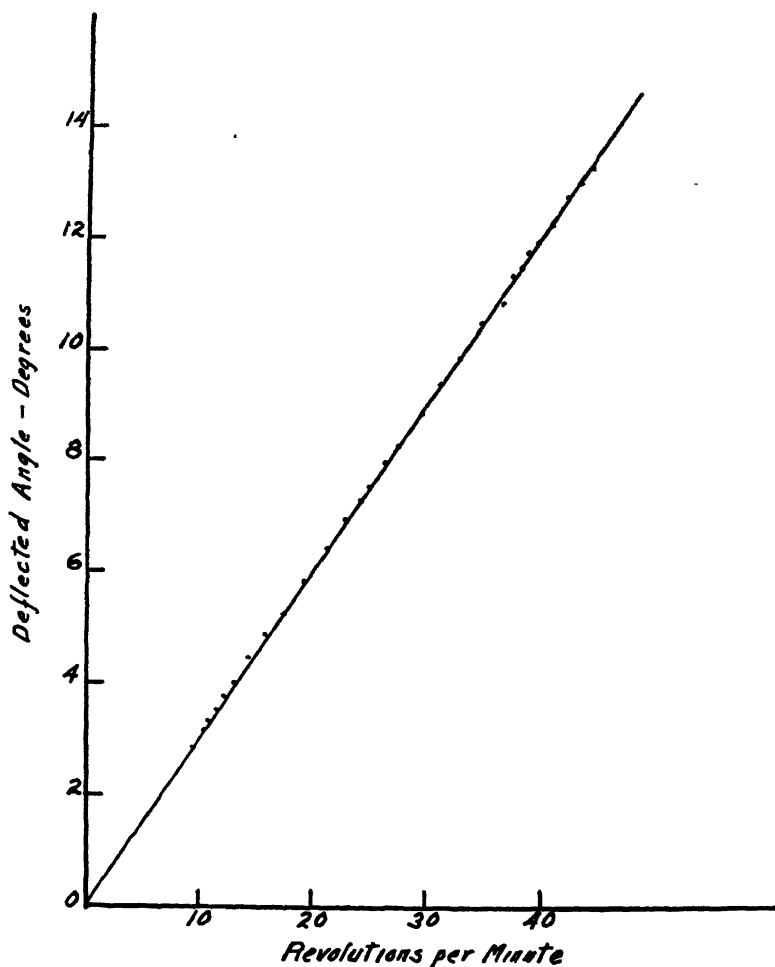


FIG. 11.—DEFLECTED ANGLE-CRUCIBLE SPEED. U. W. STANDARD CASTOR OIL SQUARE SPINDLE. 19.8° C.

and samples of them were sent to Dr. Herty of the Bureau of Mines and Dr. Lillie of the Corning Glass Co.^(24,25) for determination of viscosity by these independent laboratories, while we kept part ourselves for the same purpose.

TABLE 4.—*Typical Viscosity Data*

20 Per Cent. Anorthite, 60 Per Cent. Calcium Bisilicate, 20 Per Cent. Gehlenite

Temp., Deg. C.	Speed, R.P.M.	Initial Read., Cm.	Beam Read., Cm.	Actual Deflection	Angle ϕ , Deg.	$\eta = K \frac{\phi}{\text{speed}}$ Poises
TEST No. 1, $K = 33.44$						
1565	25.0	99.8	88.0	11.8	3.37	4.51
1526			85.2	14.6	4.18	5.59
1496			81.1	18.7	5.34	7.14
1470			76.9	22.9	6.53	8.74
1451			72.8	27.0	7.69	10.29
1442			68.5	31.3	8.89	11.90
1397			55.5	44.3	12.49	16.70
1371			41.3	58.5	16.31	20.91
1343			24.3	75.5	20.68	27.70
1325			0.0	99.8	26.52	35.48
1308	8.8		60.6	39.2	11.09	42.18
1288			54.7	45.1	12.71	48.30
1266			39.8	60.0	16.70	64.23
1244			26.0	73.8	20.25	77.86

TEST No. 2 (CHECK RUN)

1574	25.0	99.8	87.8	12.0	3.43	4.59
1552			87.8	12.0	3.43	4.59
1513			84.9	14.9	4.26	5.70
1483			79.5	20.3	5.79	7.75
1461			75.0	24.8	7.06	9.45
1412			63.8	36.0	10.20	13.65
1381			47.5	52.3	14.65	19.60
1334			22.0	77.8	21.25	28.45
1320			0.0	99.8	26.52	35.48

The analyses of the three slags, as made up for the comparison, are given in Table 5.

TABLE 5.—*Analyses of Synthetic Slags Used in Comparative Tests*

	Slag 1	Slag 2	Slag 3
SiO ₂	43.0	38.4	45.1
Al ₂ O ₃	18.4	24.5	7.2
MgO.....	7.7	13.3	6.2
CaO.....	30.8	23.8	41.5

The results reported by the three laboratories on these three different slags are shown in Figs. 12, 13 and 14. Dr. Herty's results on these three slags differ most widely from the other two laboratories. In reporting

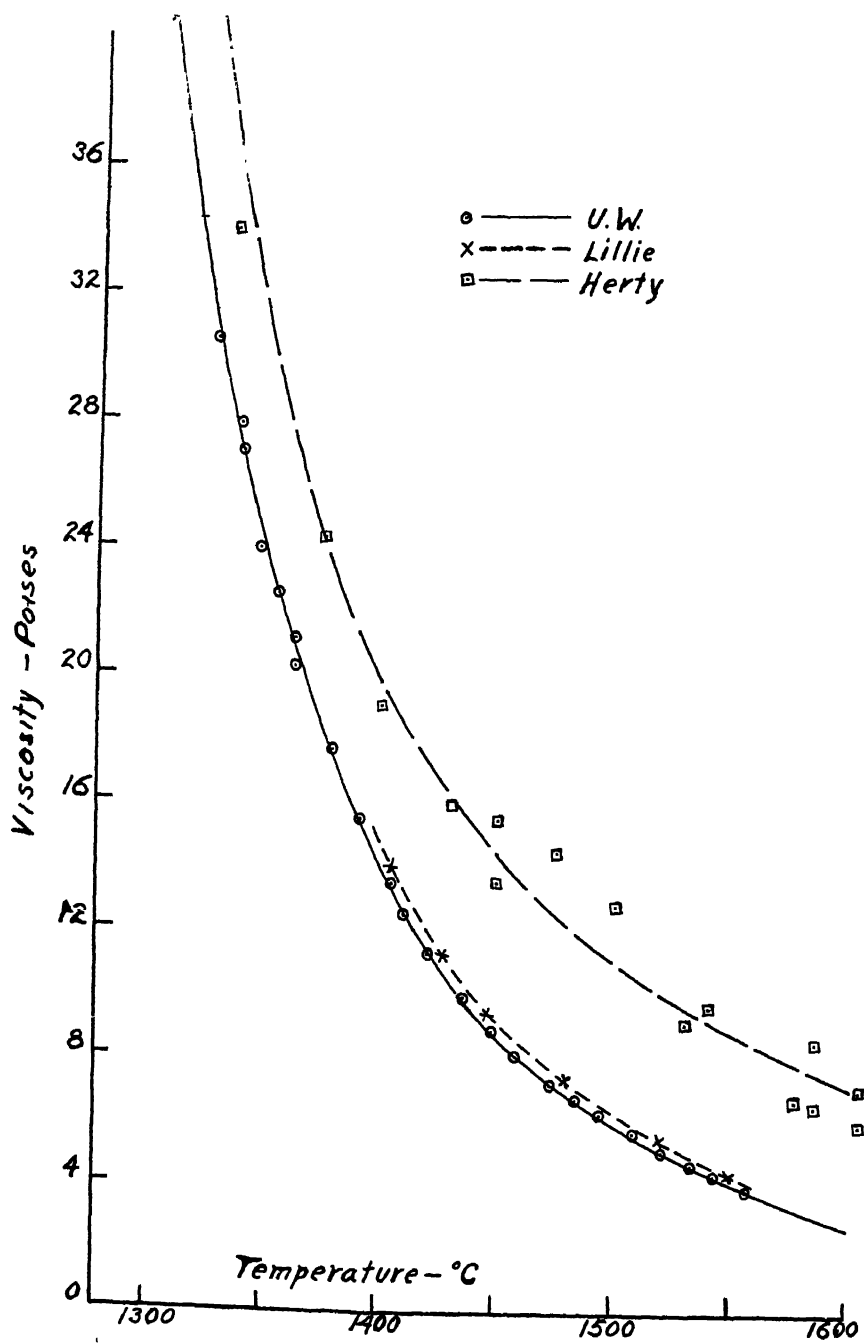


FIG. 12.—VISCOSITY OF SLAG NO. 1.

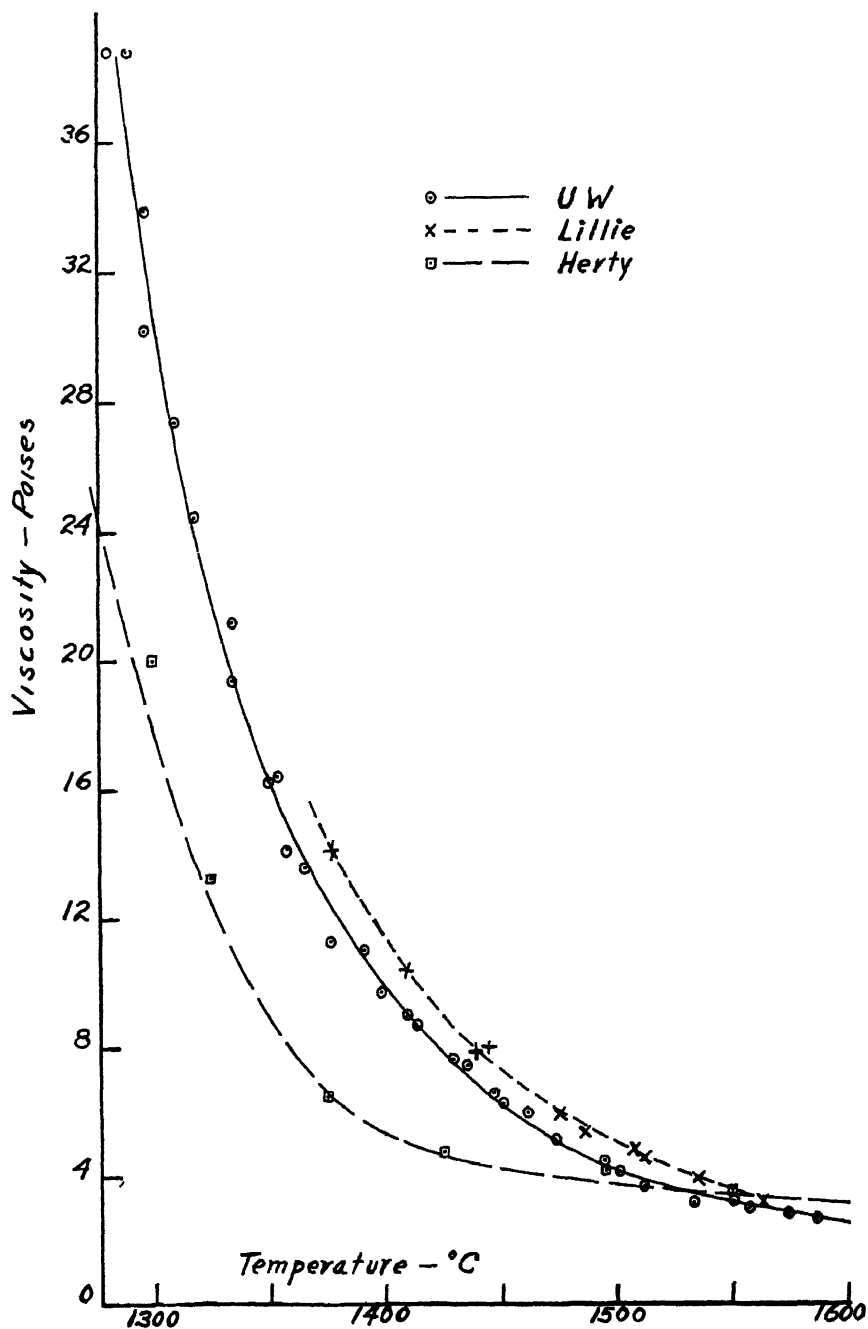


FIG. 13.—VISCOSITY OF SLAG No. 2.

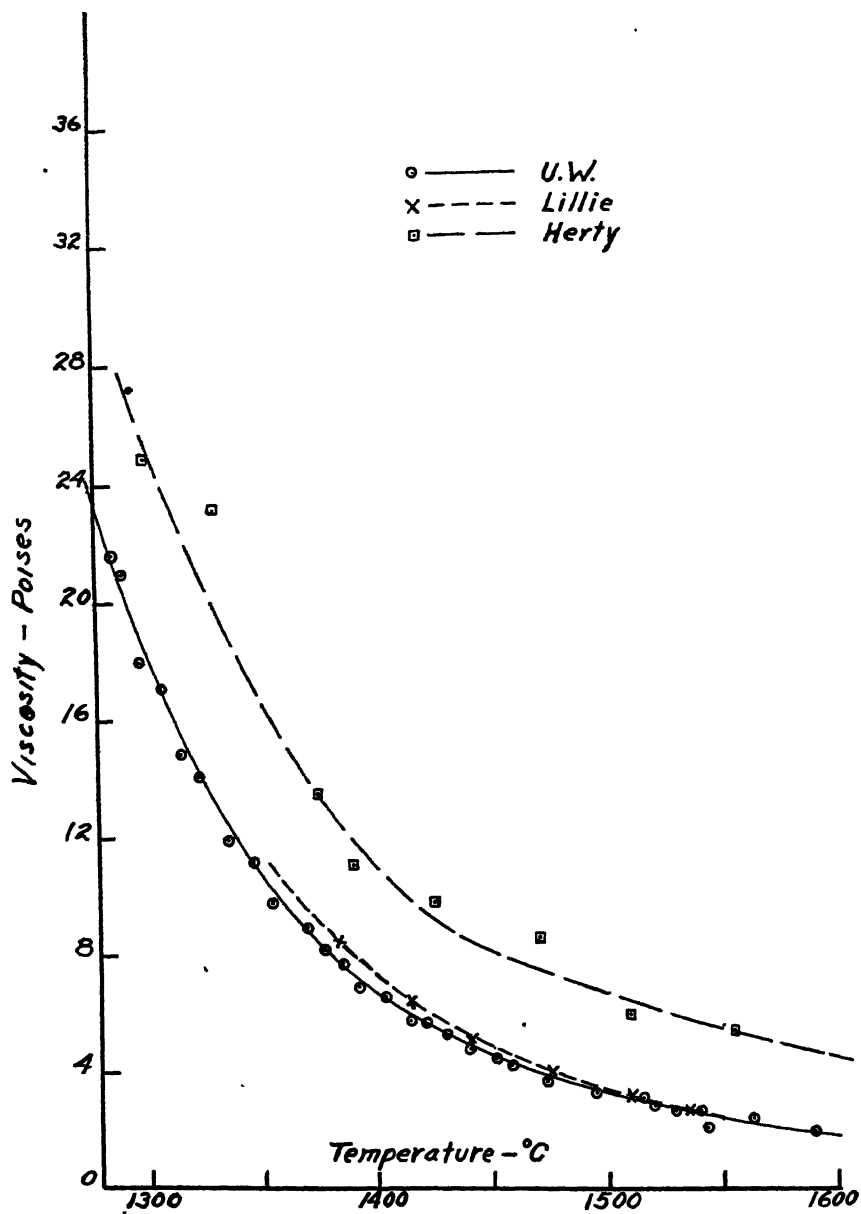


FIG. 14.—VISCOSITY OF SLAG NO. 3.

these determinations he abandoned his parabolic calibration curve and adopted a straight-line calibration curve similar to ours. As a consequence of this, all the results reported by him in *Cooperative Bulletin 47* must likewise be discarded as erroneous because they all depend on the abandoned calibration curve.

The differences between Dr. Lillie and ourselves are summarized in Table 6. These differences are so small that they are inconsequen-

TABLE 6.—*Results of Comparative Tests on Slags*

Slag No.	Viscosity, Poises	Temperature at Which this Viscosity was Determined by		Difference, Deg. C.	Difference, Per Cent.
		University of Wisconsin	Dr. Lillie		
1	13	1407	1412	5	0.36
	10	1433	1440	7	0.49
	7	1479	1486	7	0.47
	4.5	1539	1547	8	0.52
2	13	1373	1388	15	1.09
	10	1400	1416	16	1.14
	7	1439	1456	17	1.18
	4.5	1490	1517	27	1.81
	3	1564	1573	9	0.58
3	10	1358	1366	8	0.59
	7	1396	1406	10	0.72
	4.5	1454	1460	6	0.41
	3	1515	1519	4	0.26
	2.4	1550	1550	0	0.00

tial and probably are caused in largest part by the fact that Dr. Lillie employed a platinum-wound furnace with a platinum crucible and spindle, whereas we employed a graphite crucible and spindle. Dr. Lillie therefore had oxidizing conditions in his furnace whereas we had reducing conditions in ours.

DIFFUSION OF SLAG MIXTURES IN LIQUID STATE

If liquids possess the capacity for mixing in any proportion, the mixing goes on until the mixtures become uniform. Solutions of different substances, having the same degree of concentration and with other conditions similar, have been found to possess different rates of diffusion. Also, solutions of the same substance with different degrees of concentration have rates of diffusion proportional to the strength of the solution.

According to Fick's law, the rate of diffusion indicates that the quantity diffusing through a given area in a given time is proportional to the rate of change of concentration. This conclusion is confirmed in all cases.

Bowen⁽²²⁾ pointed out that the growth of crystals is accomplished largely by the diffusion of material to crystalline nuclei. Each substance has its coefficient of diffusivity, in a given medium, characteristic of the substance and determinable only by experiment. The rate of diffusion is evidently equal to the number of grams which diffuse past 1 sq. cm. of any plane in unit time when the concentration gradient normal to the plane is unity. Bowen placed a layer of diopside in the bottom of a crucible with a layer of plagioclase above it, diffusion was permitted at a constant temperature which was above the melting temperature of both layers, for a definite period. The charge was then quenched, and the composition determined at various depths by measuring the refractive index of the glass.

In all cases the actual concentration, showing a smaller gradient in the diopside-rich layers and a larger gradient in the diopside-poor layers, may be explained by assuming that the coefficient of diffusivity is not constant but is itself a function of concentration and is greater for diopside-rich mixtures than for those poor in diopside. There is a continual and very important change in the nature of the diffusion medium as time progresses, and no consistency is to be expected in the value of the coefficient of diffusivity.

Einstein⁽²³⁾ has developed for dilute solutions a theoretical relation between diffusion rate and viscosity, which makes them inversely proportional. Experimental results do not entirely confirm this theory.

The growth of crystals is itself largely dependent upon diffusion, but no quantitative estimate of the rate of growth is possible without some knowledge of the concentration gradient along which flow of material takes place.

In all of the viscosity determinations reported in this paper, no attempt was made to obtain theoretical equilibrium values. The limiting factor which makes this procedure necessary is time. The data presented, however, can be checked from different melts and by different observers.

In the original melting from the pure oxides, a homogeneous mass was obtained as shown by chemical analysis. The same mass, however, when remelted for viscosity determination, had to stand molten for 1 hr. before check determinations of viscosity could be made. We believe this is caused by the slow diffusion and solution of the slag minerals.

Melts of the pure mineral components such as gehlenite, anorthite, etc., also gave viscosity values at temperatures below their actual softening point. This, no doubt, was due to supercooling, which is quite common in slags and which is another expression of reluctance to attain

the equilibrium state. Some few slags gave the customary temperature reaction when crystallization arrested supercooling, but the majority cooled progressively without arrest to a viscosity value of 180 poises, the highest value determined in our work.

DISCUSSION OF RESULTS

The recorded data for each slag mixture were used to make temperature-viscosity curves (Fig. 15). From such curves, the viscosities at definite temperatures were taken. These temperature-viscosity relations for all of the slag mixtures examined are summarized in Table 7.

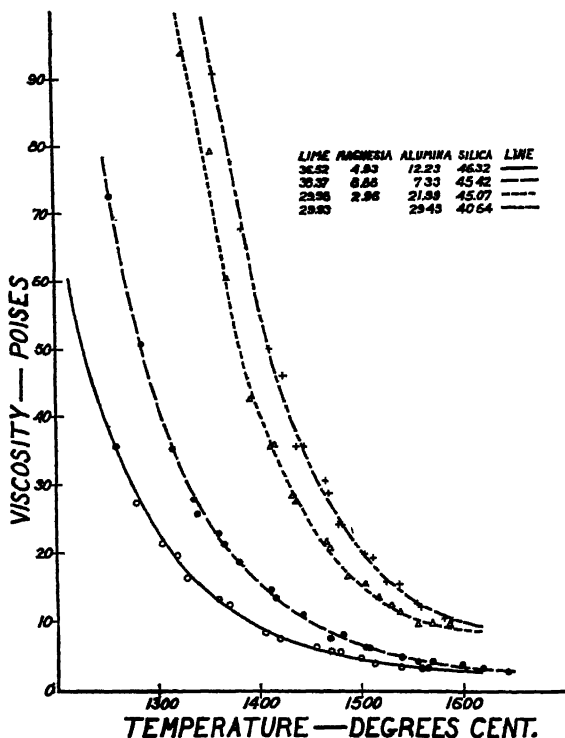


FIG. 15.—TEMPERATURE-VISCOSITY CURVES.

The temperature-viscosity relations of slags in the ternary system silica-alumina-lime do not correspond to the work Feild and Royster reported in their Slag Viscosity Tables.⁽¹¹⁾ A comparison of the two investigations is readily made by plotting equal viscosity lines in the area covered by the two investigations. Plotting equal viscosity lines at 1600° C. (Fig. 16) from data taken from the Slag Viscosity Tables and comparing them to the superimposed equal viscosity lines taken from the reported results of this investigation, there is found little in common

TABLE 7.—Viscosity Data

MINERAL COMPOSITION %			CHEMICAL COMPOSITION %				VISCOSITY IN POISES AT TEMPERATURE °C.									
			CaO	MgO	Al ₂ O ₃	SiO ₂	1650	1600	1550	1500	1450	1400	1350	1300	1250	
100 D			48.28			51.72	2.38	2.40	2.73							
100 A			41.14			44.07		1.40	1.77							
100 M			40.91			42.91	2.72	3.54	4.95	2.30	3.18	4.53	6.02	28.00		
100 B			20.16			43.19		25.00	38.00	60.50	111.00					
100 Q			35.84			38.39		1.13	1.20	1.74						
100 K			25.90			55.48		1.80	1.40	1.86						
90 D	10 M		48.74			48.74		1.82	2.68	3.80	5.21	7.36				
80 D			46.81			45.75		1.00	2.08	3.40	5.00	7.07	10.25	19.20		
70 D	30 M		46.07			42.78		3.20	3.57	4.42	6.38	10.17	15.78	25.30		
65 D	35 M		45.70			41.29		2.40	3.15	4.55	6.90	10.40	17.40	31.40		
60 D	40 M		45.33			39.80		2.33	3.16	4.45	6.75	10.80	18.25	32.00		
50 D	50 M		44.99			36.82		2.10	3.35	5.65	7.50	11.30	17.65	32.00		
40 D	60 M		43.86			33.83		2.28	3.25	4.80	7.30	11.70				
20 D	80 M		42.38			2.88		3.12	4.20	7.00	2.77	3.76	5.95	17.00		
80 A	20 M		41.09			35.64		1.72	1.45	2.20	2.96	4.05	5.85	16.00		
74 A	25 M		41.08			36.31		1.06	1.52							
60 A	40 M		41.05			35.21		2.15	2.60	3.35	4.40	6.15	9.55	15.75		
40 A	60 M		40.00			36.77		2.41	2.66	3.64	5.20	27.00				
20 A	80 D		40.96			28.34		2.48	2.73	3.59	4.00					
			46.85			30.19		1.60		2.95						
35 A	65 D		45.78			43.04		1.50	1.86	2.40	3.19	4.41	6.50	32.00		
50 A	40 B		44.71			41.90		1.20	1.94	2.10	2.95	4.19	6.15	10.60		
60 A	43 B		44.25			41.59		1.40	1.60	2.39	3.21	4.43	6.45	12.00		
			44.10			41.13		0.80		1.65	1.95	2.72	3.96	8.60		
80 A	20 D		42.57			45.60		1.00	1.28	1.77	2.40	3.35	5.84	16.00		
20 A	60 B		24.36			43.36		9.15	12.90	20.85	36.70	60.50	112.50	65.90		
40 A	50 B		28.55			43.54		6.00	7.90	14.45	22.65	36.70	65.90	120.00		
50 A	60 B		30.65			43.63		4.10	5.40	9.90	14.50	23.60	42.00	75.20		
60 A	40 B		32.75			43.72		3.70	4.70	6.35	9.05	13.95	21.20	35.25		
70 A	30 B		34.85			43.81		1.98	2.65	3.60	5.05	7.41	11.19	18.30		
85 A	15 B		37.99			43.94		1.01	1.28	1.80	2.60	3.95	6.20	24.00		
20 M	80 B		24.31			38.93		1.60	2.10	29.45	48.90	90.00				
40 M	60 B		28.46			36.86		13.40	17.25	20.00	33.75	58.50	109.50	180.00		
51.3 M	48.7 B		30.80			32.68		16.15	14.00	24.50	38.25	61.00	100.05			
60 M	40 B		32.61			30.42		8.00	9.45	12.50	19.50	32.50	74.00			
80 M	20 B		36.76			26.16		5.08	5.80	45.00						

TABLE 7.—(Continued)

MINERAL COMPOSITION %			CHEMICAL COMPOSITION %			VISCOSITY IN POISES AT TEMPERATURE °C.									
			CaO	MgO	Al ₂ O ₃	SiO ₂	1650	1600	1550	1500	1450	1400	1350	1300	1250
2QD	80.B		25.78		29.32	44.90		22.60	23.00	27.00	40.50	71.80	77.55	150.00	
4QD	60.B		31.41		21.99	46.60		10.50	12.65	16.70	22.25	44.90	44.90	150.00	
51.7D	48.3B		34.70		17.70	47.60		1.50	12.10	16.50	26.00	40.25	35.75	60.13	110.00
6QD	40.B		37.03		14.66	48.31		3.35	4.25	5.17	7.00	11.10	7.00	40.00	
8QD	20.B		42.66		7.93	50.01		1.24	1.32	2.35	2.50	4.35	3.48	7.00	
8Q.A	20.0		40.08	16.99		42.93		1.00	1.78	1.80	2.10	3.48	6.40	60.00	
60.A	40.0		37.96	21.38		41.60	0.80	1.00	1.41	1.60	2.10	4.00	8.30	60.00	
40.A	60.0					40.66			1.08	1.65	4.00	9.50			
2Q.A	80.0		36.90	23.70	39.53	33.59		1.10	1.08	2.67	3.73	5.39			
20.M	80.0		36.84	22.63	7.44	33.59		0.77	1.25	2.00	3.95	6.32			
40.M	80.0		37.87	15.46	14.87	31.80		1.25	1.90	2.67	3.73	5.39			
60.M	40.0		36.88	10.31	28.31	28.50	1.34	1.58	2.00	2.67	3.73	5.39			
8Q.M	20.0		38.90	5.15	29.74	25.21	1.60	2.28	3.10	4.22	8.00	10.20			
20.B	80.0		35.70	20.62	7.33	39.35		1.52	1.98	2.67	3.73	5.39			
40.B	80.0		25.57	15.46	14.66	40.31		2.45	3.60	5.00	7.00	10.20			
60.B	40.0		26.43	10.31	21.99	41.27		4.60	6.50	9.65	13.00	19.60			
8Q.B	20.0		23.30	5.15	29.32	42.23		10.00	13.70	19.65	33.00	55.75			
15.A	85.K		28.19	18.05		53.76		1.90	2.15	2.60	3.94	6.40			
30.A	70.K		30.47	17.47		52.06		1.08	1.32	1.73	2.31	3.31			
42.A	58.K		32.30	17.01		50.69		1.28	1.41	1.80	2.45	3.63			
50.A	50.K		33.52	16.70		49.78		1.35	1.70	2.30	3.20	4.60			
65.A	35.K		35.81	16.13		48.06		1.30	1.62	2.15	2.91	4.00			
80.A	20.K		38.09	15.56		46.35		0.78	1.12	1.65	2.45	3.60			
20.D	80.K		30.38	14.90		54.72		1.55	1.97	2.59	3.43	4.82			
40.D	60.K		34.25			53.98		1.62	2.00	2.60	3.35	5.05			
50.D	50.K		37.09	9.31		53.60		1.75	2.12	2.75	3.61	5.07			
60.D	40.K		33.33	7.45		53.22		2.00	2.43	3.15	4.13	5.75			
80.D	20.K		43.80	3.72		52.48		2.39	2.95	3.97	5.41	7.55			
20.B	80.K		24.75	14.90	7.33	53.02		1.85	2.28	3.03	4.40	6.90			
20.B	80.N		22.92	13.58	24.50	36.99		1.40	2.05	3.01	4.60	6.85			
40.B	60.N		22.23	10.19	27.54	40.04		3.85	5.00	6.80	9.65	14.50			
60.B	40.N		21.64	16.79	30.58	41.09		5.25	7.50	10.65	15.70	25.35			
20.0	80.0		26.06	18.74	17.17	38.03		1.27	1.59	2.10	2.95	4.44			
40.0	60.0		26.50	20.50	12.88	38.12		0.98	1.27	1.78	2.52	3.64			
60.0	40.0		30.96	22.25	8.59	38.21		0.70	0.80	1.07	1.60	4.00			
80.0	20.0		33.39	24.01	4.29	38.31		0.68	0.80	1.20	3.45				

TABLE 7.—(Continued)

MINERAL COMPOSITION %			CHEMICAL COMPOSITION %			VISCOSITY IN POISES AT TEMPERATURE °C.									
			CaO	MgO	Al ₂ O ₃	SiO ₂	1650	1600	1550	1500	1450	1400	1350	1300	1250
20M	80N		87.07	13.59	24.60	34.74		1.40	1.90	2.65	3.67	5.30	8.30	17.60	
40M	40N		56.45	16.18	24.76	31.53		2.45	3.36	3.35	4.76	7.90	16.00		
75S3S	2475D		55.85	6.79	30.69	44.15		1.14	1.80	15.00	8.50				
3820S	6380D		51.98			48.08		1.70	2.47	3.48	8.30				
3820S	2400E		47.99			52.01		2.77	3.63	4.78					
8123D	624J		44.06			55.94		2.80	4.08	5.78					
8112D	1058J		42.13			57.87		3.95	10.57	13.45	45.00				
7498D	2502J		36.80			63.20		15.00	21.50	34.00	52.75	79.50	108.40		
6239A	2400E	13.11 O	45.80	2.68		41.12		0.87	1.07	1.08	2.50	15.10	25.00	35.00	
20A	20B	60.0 D	41.23	2.96	7.93	48.18		3.48	5.16	7.20	10.15	41.00	78.25	140.00	
20A	60B	20.0 D	28.98		21.99	45.07		6.30	10.00	15.35	24.40				
60A	20B	20.0 D	38.37	8.88	7.33	45.42		2.80	3.45	4.50	6.30	9.20	14.30	23.35	39.00
3333A	3333B	33.33 D	36.52	4.93	12.23	46.32		3.40	4.50	6.60	9.85	15.65	24.45	42.00	
3333A	3333B	33.33 K	28.07	11.14	12.87	39.11	2.75	3.05	4.00	5.23	7.01	9.95	14.80	23.15	
20A	60B	20.0 M	28.50	2.96	23.45		8.00	8.00	10.60	17.20	28.60	46.15	95.00	200.00	
3333A	3333B	33.33 M	34.07	4.39	24.41	36.39		6.50	8.20	11.40	15.75	23.80	41.20	81.00	
20A	20B	60.0 O	33.76	18.42	7.35	40.49		1.72	2.21	3.01	4.19	5.91	8.55	40.00	
60A	20B	20.0 O	27.49	8.11	21.99	42.11		5.75	7.35	10.20	15.40	24.25	39.60	68.25	
20A	20B	20.0 O	35.88	14.03	7.33	42.76		2.00	2.28	2.80	3.60	5.00	7.70	22.00	
3333A	3333B	33.33 O	32.38	13.62	12.22	41.88		2.96	3.63	4.86	7.05	10.56	15.30	22.70	35.75
20A	20B	40.0 K	33.42	14.13	26.45			2.41	2.81	3.45	4.32	5.60	7.80	40.00	
20A	20B	40.0 K	42.50	12.60	21.40	50.94		2.68	3.25	4.50	5.97	9.50	15.40	27.78	
20A	20B	20.0 K	42.38	6.68	20.94			2.10	2.68	3.54	4.80	6.90	10.20	20.60	
60A	20D	20.0 K	39.52	12.60		47.88		1.99	2.39	3.00	3.82	5.21	8.80	23.00	
3333A	3333B	33.33 K	38.44	11.14	22.31	50.42		3.71	4.99	5.60	7.40	10.02	14.00	24.00	
20A	20D	20.0 M	42.43	2.96	36.30	44.23		3.60	4.88	6.45	9.40				
20A	60D	20.0 M	45.38	2.96	7.44			2.55	3.20	4.07	5.47	7.84	11.80	18.00	
60A	20D	20.0 M	45.52	8.87	7.44	41.18		1.54	2.09	2.77	3.80	5.30	7.83	32.00	
3333A	3333B	33.33 M	43.44	4.93	12.39	39.24		2.60	3.54	4.78	7.00	10.73	17.58	30.00	
3333A	3333B	33.33 S	46.30	6.30	44.50			2.28	2.70	3.37	4.25	5.70	8.04	50.00	
20A	20M	60.0 O	37.91	18.42	7.44	36.23		1.20	1.52	2.00	2.77	4.30			
60A	20M	20.0 O	40.03	14.03	7.44	38.60		2.97	3.61	4.40	5.56	9.30	25.34	41.75	
3333A	3333B	33.33 J	39.31	15.07	12.39	42.79		2.12	2.47	3.08	4.20	6.32	15.00	70.00	
3333A	3333B	33.33 J	34.90	24.90	12.81	55.29		9.20	14.40	20.40	23.80	47.00	75.70		
50A	3755D	12.45J	28.27		18.33	53.46		28.20	36.30	51.00	80.90				

TABLE 7.—(Continued)

MINERAL COMPOSITION %			CHEMICAL COMPOSITION %			VISCOSITY IN POISES- AT TEMPERATURE °C.									
			CaO	MgO	Al ₂ O ₃	SiO ₂	1650	1600	1550	1500	1450	1400	1350	1300	1250
3333 B	3333 D	3333 K	31.44	6.80	12.81	50.15		3.30	4.70	6.70	9.75	14.90	24.30	40.80	72.40
20 B	20 D	20 M	36.23		12.64	32.13	4.70	6.04	8.20	12.18	19.85	36.00			
2540 B	4578 D	2582 M	41.18		14.77	44.06		4.05	4.95	6.50	10.90	18.40	26.25	44.40	73.60
			36.06		24.00	42.00		5.40	7.70	10.75	15.90	28.40	46.70	78.30	
60 B	20 D	20 M	29.93		23.43	40.44		9.85	13.40	20.75	33.00	57.85	99.00	87.25	
3333 B	3333 D	3333 M	36.45		36.94	36.94		6.20	8.05	11.90	16.90	27.25	42.60	72.25	
3333 B	3333 M	60 D	29.83	5.66	31.76	34.55		3.95	5.20	7.65	14.20	26.00	35.75	51.15	
20 B	20 D	20 M	33.78	15.46	44.77	36.65		7.65	2.20	3.08	4.20	6.05	9.15	15.25	
20 B	60 M	20 O	35.75	5.15	23.04	23.46		2.70	3.70	5.50	7.75	33.20	57.85	98.50	
3333 B	3333 M	3333 O	35.30	5.15	23.46	37.97		5.70	7.90	12.15	20.25	32.20	47.60	75.75	
3333 B	3333 M	3333 O	26.54	14.25	24.61	34.60		2.70	5.80	3.53	6.15	12.70	21.65	34.08	
			45.17		19.37	28.20	2.50	2.08	2.81	3.93	5.15	9.18	15.05		
3747 D	1252 J	5001 K	31.05	9.31	53.64	53.64		3.85	4.18	5.00	6.84	9.98	14.61	24.00	
5631 D	833 J	3336 K	45.79	6.21	47.00	47.00		2.75	3.45	4.90	6.20	9.10	13.70	20.25	
5674 D	7162 M	2153 S	45.17		11.80	41.00		3.00	3.00	3.47	4.42	5.78	7.60	14.30	
					26.63	28.20		5.10	4.20	6.25					
1357 D	4325 M	4318 S	49.44		16.08	34.48		1.45	2.00	3.10	4.85	7.27	11.25	17.50	
2266 D	2166 M	5388 S	46.57		2.34	46.57		2.82	2.00	2.80	5.15				
309 E	1650 M	7443 S	36.07		6.16	46.57	3.00	4.55	34.60						
1743 E	3819 M	4448 S	52.87		14.19	32.94		3.00	36.80	6.05					
2735 E	6650 M	615 S	48.60		24.74	24.66	1.50	3.19	4.00						
2632 E	3607 M	4333 S	53.45		13.41	33.14	2.30	2.30	2.90	3.60	5.00	7.90	19.10		
4282 D	2388 M	4333 S	44.87		8.88	41.25		2.40							
2212 E	6969 O	819 S	47.85	10.31	41.84	41.84		1.06	1.38	1.82	4.77	4.24	6.25		
3333 B	3333 N	40 O	35.45	14.10	16.03	36.75		0.60	2.80	2.97	4.08	5.80	8.25		
60 M	20 N	20 O	36.44	8.68	26.60	36.75		2.08	2.90	3.80	5.28	7.75	8.25		
1666 A	1666 B	1666 D	31.21	11.78	6.11	50.90		3.00	3.16	3.49	4.62	7.01	10.28	15.80	
1666 A	1666 B	1666 D	35.67	5.97	49.45	49.45		1.90	2.43	3.74	5.67	8.43	12.50	22.80	
1666 A	1666 B	1666 D	56.29	0.50	18.32	46.81		4.40	2.20	10.80	16.70	25.60	42.50	74.60	
			56.29	0.50	6.11	47.10		2.19	2.90	3.80	5.12	7.07	10.40	20.60	
25 A	25 B	25 D	33.97	8.95	9.16	48.42		3.40	3.88	4.68	6.13	8.88	13.60	21.95	
1666 A	1666 B	1666 D	38.71	2.47	24.70	34.12		2.93	3.75	4.95	8.26	13.15	18.65	30.60	
50 A	50 B	50 D	47.18	2.47	12.30	47.18		3.60	4.51	5.80	7.88	11.87	19.15	32.20	
			38.80	7.39	12.50	41.51		3.80	4.68	6.08	8.40	12.71	19.15		

between the two sets of curves except in the area bounded by 7 to 19 per cent. alumina, 38 to 50 per cent. silica and 38 to 47 per cent. lime, where slags are fluid and the numerical values of viscosities are practically identical. Our investigations failed to show the rapid increase in slag viscosities on approaching a composition of approximately 42 per cent. silica, 20 per cent. alumina and 38 per cent. lime. From the equilibrium diagram for the system calcium bisilicate-gehlenite-anorthite, there seems no apparent reason for the rapid increase in viscosity at that point other than that this composition is the composition of the ternary eutectic for the system. The investigation reported in this paper does not show the rapid rise in viscosity of slags containing more than 49 per cent. lime and 11 to 16 per cent. alumina. We have found these slags very fluid. It was not until the lime had increased above 55 per cent. that the slags became more viscous.

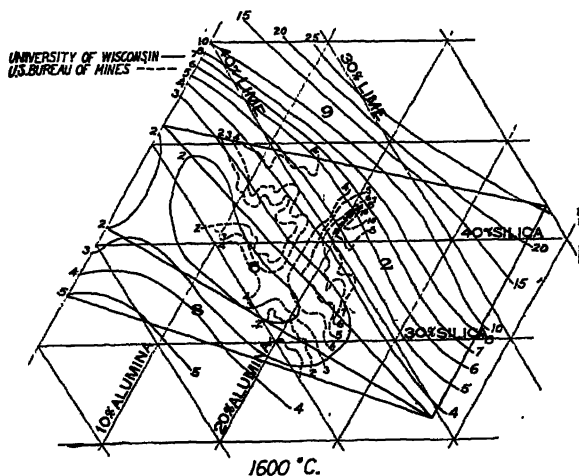


FIG. 16.—VISCOSITY DATA, PLANE OF 0 PER CENT. MAGNESIA.

The authors feel that the possible causes may be sought for in the following differences in technique and operation.

The gran-annular type of furnace used by Feild and Royster gives off large volumes of gases while it is heating. Presumably such gases interfere with temperature measurements and may cause fluctuations in spindle deflections. No temperature corrections for non-black-body conditions were reported. The centering of the spindle in the gran-annular furnace is difficult because of the heat radiated from the hot walls and shell. How the spindle was centered was not clearly described in their papers. The high-frequency furnace lends itself to rapid and accurate centering of the suspension system without discomfort to the operator.

No mention was made by Feild and Royster of obtaining an emissivity value for their furnace. In our work an emissivity value was obtained by calibration of the optical pyrometer in the furnace against standard thermocouples.

Another factor of importance was the different spindles used in the investigations. Feild and Royster used a cylindrical spindle while a square prism was used in our work. (See footnote 2, page 93.) We found that the cylindrical spindle gave erratic values.

Feild and Royster reported that the viscosity determinations were begun shortly after the charge was molten. We have found that slow diffusion in a mixed charge made constant viscosity readings at a given temperature an impossibility until the slag had been molten for some time. It would seem probable, then, that the improvements in apparatus design and its manipulation which we incorporated lend themselves to greater accuracy in measuring the viscosity of molten slags.

SUMMARY

The apparatus for determining the viscosity of molten slags and the method of operation is described.

All data obtained on temperature-viscosity relations for slags in the silica-alumina-lime-magnesia system are summarized.

A comparison is made of the results reported in the work of Feild and Royster and the data reported in this investigation.

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[For discussion, see page 135.]

Effect of Magnesia on Slag Viscosity*

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(New York Meeting, February, 1931)

THE method of obtaining the data on which this paper is based is explained in detail in the paper on Determination of Viscosity of Iron Blast-furnace Slags.¹ The work was made possible by a grant of funds from Engineering Foundation, and it gives the results now obtained, continuing the general subject of our previous work and reported in former papers.²

The data experimentally obtained are in the form of a temperature-viscosity curve for any slag of particular composition. (See Fig. 1.) From these curves, the viscosity of a slag of a definite composition and at a definite temperature is taken off and is plotted on a plane triaxial diagram showing compositions of silica lime and alumina on a plane representing constant-magnesia content (Fig. 4).

The temperatures at which these results were plotted are 1300°, 1350°, 1400°, 1450°, 1500°, 1550° and 1600° C. and since the constant magnesia plane sections were an even 1 per cent. magnesia apart, magnesia analyses not of even unit magnesia composition were projected to these even unit magnesia planes. For example, 1.78 per cent. magnesia and 2.35 per cent. magnesia were projected to the 2 per cent. magnesia plane.

The triaxial diagrams on which this first plotting was made were drawn on celluloid sheets, a transparent material on which it was easy to draw. When all the experimental work was plotted on celluloid in this way, the sheets representing a definite temperature were stacked in the proper order and were examined by transmitted light. Where

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¹ R. S. McCafferty, C. H. Lorig, I. N. Goff, J. F. Oesterle and O. O. Fritsche: Determination of Viscosity of Iron Blast-furnace Slags. See page 86.

² R. S. McCafferty and J. F. Oesterle: Desulfurizing Power of Iron Blast-furnace Slags. *Trans. A. I. M. E.* (1923) 69, 606.

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necessary, corrections were made in the position of the isoviscosity lines, but care was taken not to violate the original data in any way. When this was completed for sheets representing a particular temperature, sections were cut at right angles through the planes and these sections were examined to see whether they gave fair lines. In case they did not, the celluloid sheets were again corrected without violation of the original data, new sections were cut and re-examined until all gave fair lines. Then the isoviscosity lines were copied on paper in the final form.

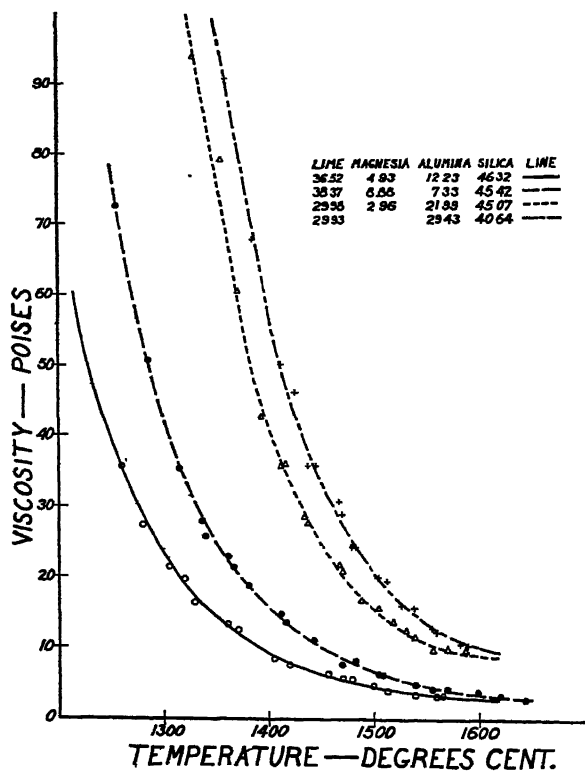


FIG. 1.—TEMPERATURE-VISCOSITY CURVES.

In this paper we have selected part of our data, which we believe will be entirely satisfactory for practical purposes, so as to reduce to a minimum the number of illustrations necessary to present the results of the work. Figs. 4 to 18 inclusive show the viscosity of any silica-alumina-lime-magnesia composition, including all the ranges of blast-furnace slag composition and considerably beyond, at temperatures of 1400°, 1500° and 1600° C. and on planes of constant magnesia content of 0, 5, 10, 15 and 20 per cent. To obtain results from which selections could be made as above, it was necessary to plot magnesia contents not

more than 1 per cent. apart and at temperatures of 1300°, 1350°, 1450° and 1550° C. Also, it was necessary to plot the viscosities at the 1 per cent. magnesia planes intermediate between the 5 per cent. planes herein and at temperatures of 1300°, 1350°, 1450° and 1500° C., none of which are included in this paper.

In addition to the diagrams giving the viscosities at definite temperature, we include a series of diagrams, Figs. 19 to 23, inclusive. Each diagram shows the viscosities at three different temperatures, 1400°, 1500° and 1600° C., so that the effect of temperature change on a slag of definite composition can be studied conveniently.

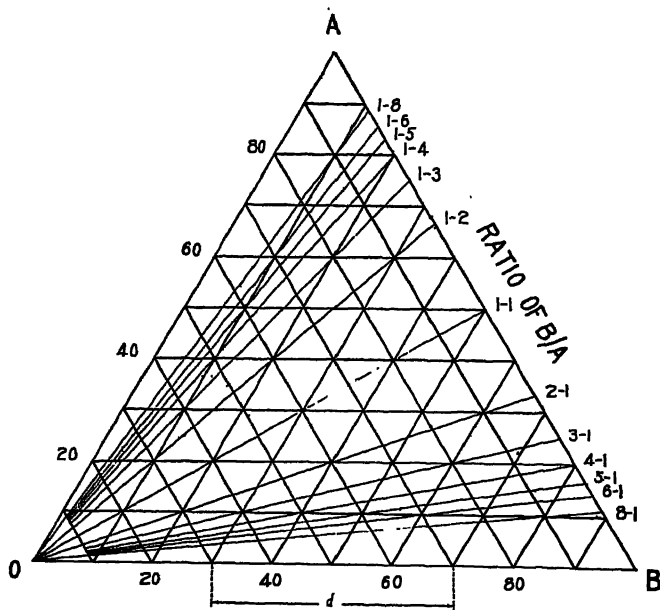


FIG. 2.—CELLULOID SCALE.

Perhaps the most striking fact observable in these viscosity diagrams is the effect of magnesia in reducing differences of viscosity in slags that consist of silica, alumina and lime with varying magnesia content. If the diagram of 0 per cent. magnesia at any one temperature, say 1500° C. (Fig. 9), is compared with Fig. 11, which gives the viscosity at 1500° C. for 10 per cent. magnesia, it will be seen that the "contours" (isoviscosity lines) show a much flatter topography (less viscosity change) at 10 per cent. magnesia than they do at 0 per cent. magnesia. Similar comparisons made at other temperatures give the same result. In other words, with a higher magnesia content there is less change in viscosity when silica, alumina and lime vary among themselves than there is with a lower magnesia content.

It would appear that this fact alone would have an important bearing on blast-furnace practice. It is generally believed that slag viscosity plays an important part in the desulfurization that takes place in the blast furnace. It is impossible to prevent variations in the silica-alumina-lime content of the slag, because these materials will vary in the charge, but with higher magnesia content the effect of this silica-alumina-lime variation does not change the viscosity nearly so much as it does with lower magnesia. Thus one of the variables of furnace operation is mini-

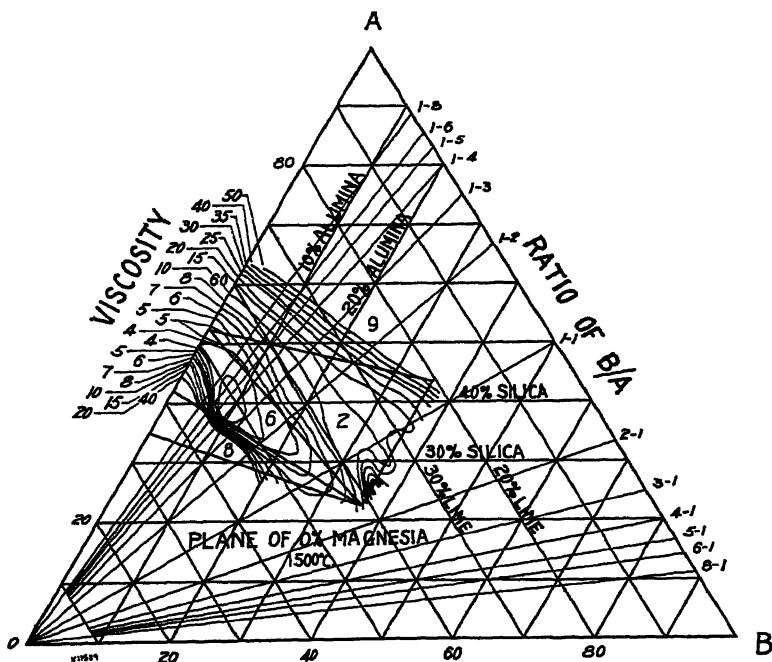
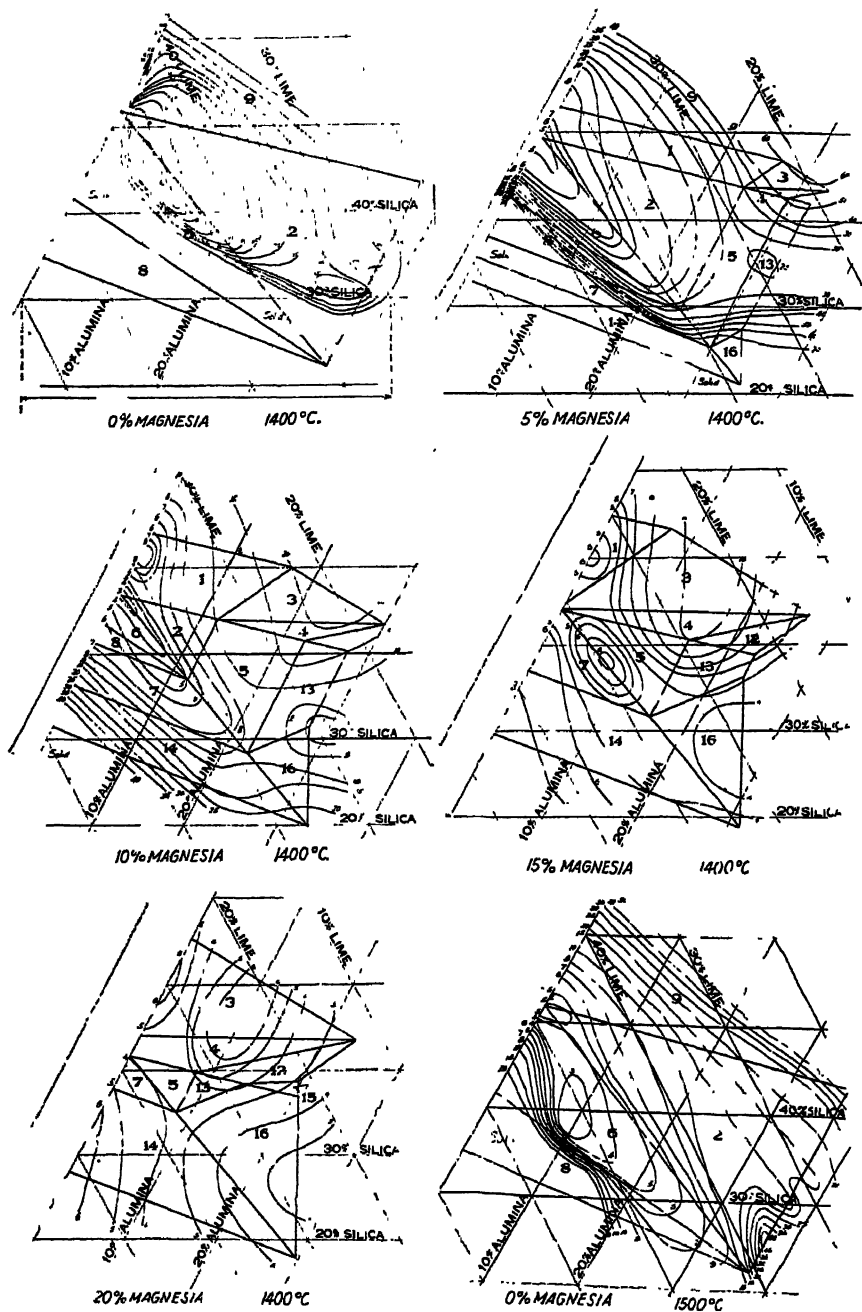


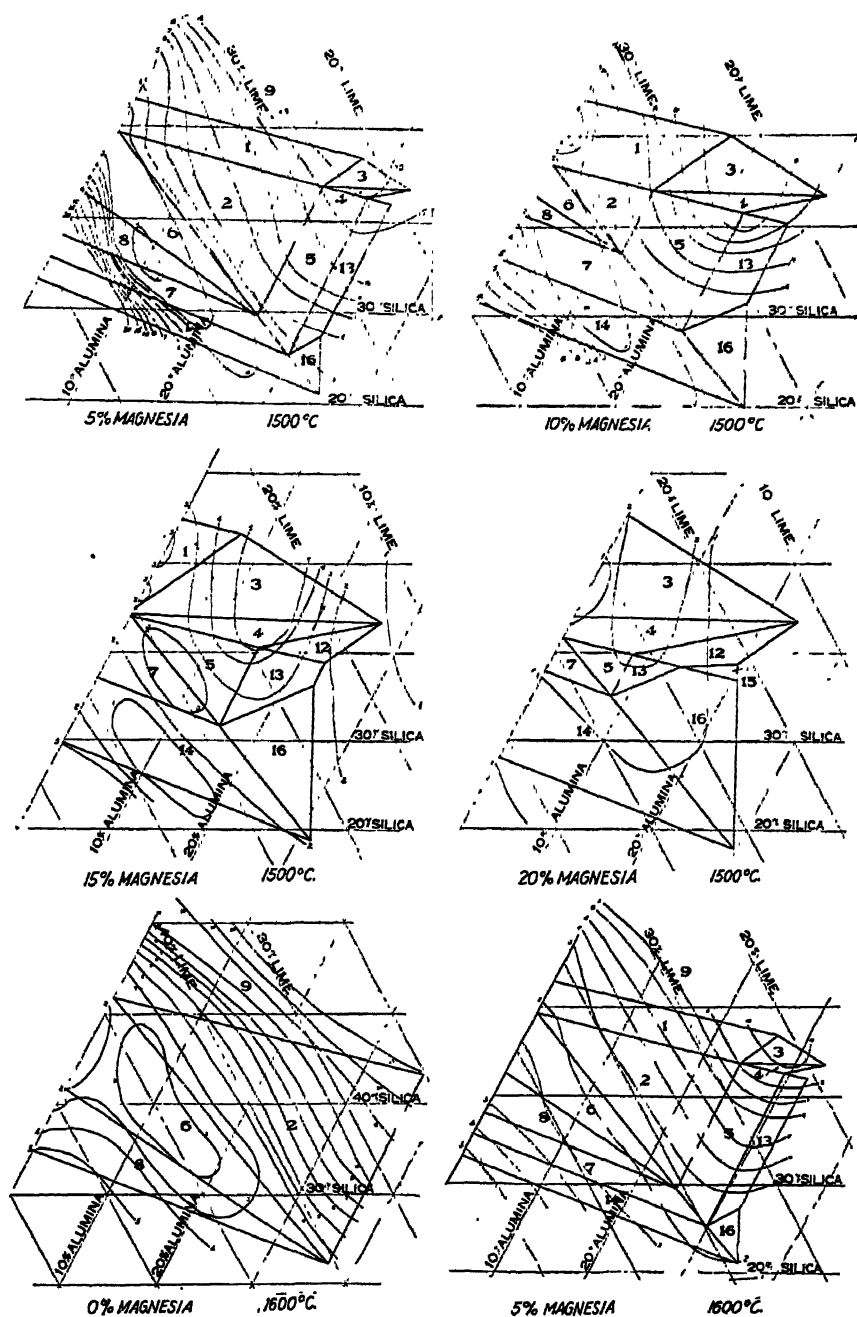
FIG. 3.—CELLULOID SCALE APPLIED TO FIG. 9.

mized, which should result in greater regularity of operation and uniformity of furnace product.

Generalizations regarding viscosity over the whole field of composition of blast-furnace slags cannot be made, but the diagrams do furnish the data for comparison and study throughout the whole of this range. A very convenient means for this detailed study of the diagrams is by the use of a transparent triangle of celluloid or of tracing linen or tracing paper. The graduations are drawn on the triangle to the same scale as the viscosity diagrams. A recommended method of graduating this scale is shown in Fig. 2. One set of lines is parallel to the side AB. These lines indicate 10 per cent. variation of the O constituent. From the apex O a series of lines radiate to the AB line and are marked with their



FIGS. 4-9.—VISCOSITY OF ANY SILICA-ALUMINA-LIME-MAGNESIA COMPOSITION, INCLUDING ALL RANGES OF BLAST-FURNACE SLAG.

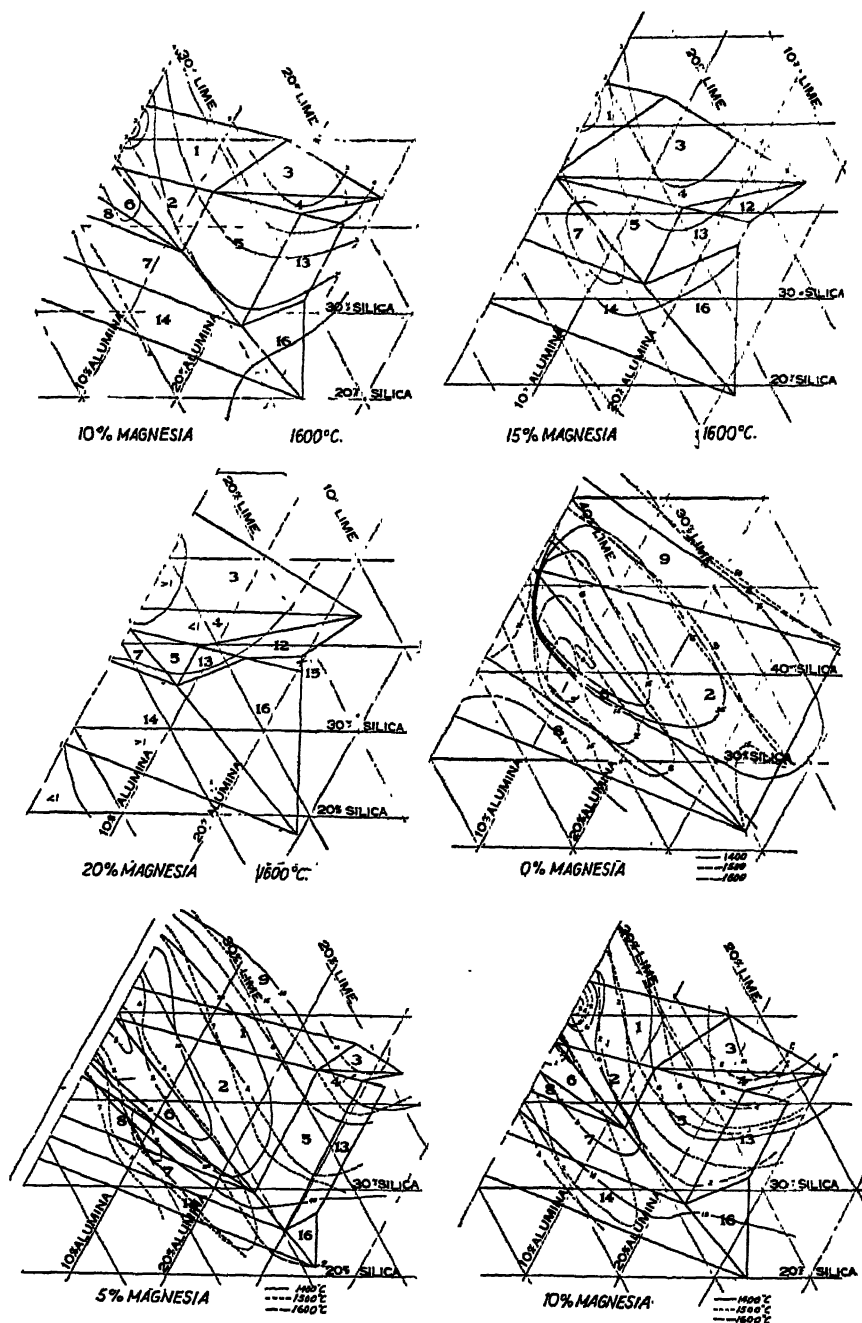


FIGS. 10-15.—VISCOSITY OF ANY SILICA-ALUMINA-LIME-MAGNESIA COMPOSITION, INCLUDING ALL RANGES OF BLAST-FURNACE SLAG.

respective ratios. Along one of these radial lines, there is a constant ratio of the *B* constituent to the *A* constituent. In constructing a transparent scale, it is important that the scale be of the correct size to use on the diagrams and the distance *d* in Fig. 2 should be exactly the distance *d* in Fig. 4. If one of these transparent scales were superimposed on a diagram where silica increased from the bottom up to *A*, where alumina increased from the left side to the lower right-hand end of base *B*, and where lime increased from the right side to the lower left-hand end of base *O*, then the lines parallel to *AB* on the scale would indicate percentages of lime 10 per cent. apart and the radial lines from *O* will represent points along which the ratio of alumina to silica is indicated by the ratio marked on the particular line. Fig. 3 shows such a scale superimposed on a silica-alumina-lime diagram in the manner referred to above. The particular silica-alumina-lime diagram selected for this purpose is Fig. 9, which gives viscosities of 0 per cent. magnesia slags at 1500° C. Since the *A* component in this diagram is silica, the 20 per cent. *A* component line of the transparent scale should be superimposed on the 20 per cent. silica line of the diagram. Similarly the *B* component in this case is alumina and the left side line of 0 per cent. *B* component should at the same time be superimposed on the 0 per cent. alumina line of the diagram. Then the ratio lines on the transparent scale indicate alumina-silica ratios on the diagram and the percentages of lime are read from the diagram. By superimposing a proper transparent scale over Fig. 9, which condition is represented in Fig. 3, it will be noted in the case of slags of about 40 per cent. lime and 0 per cent. magnesia, that an alumina-silica ratio of 1:2 to 1:8 gives practically no change in viscosity. This means that if the lime and magnesia are kept constant as they were in this case at 40 and 0 per cent., the ratio of alumina to silica can vary within wide limits in this part of the diagram with very little variation in the viscosity. It also means that in this part of the diagram, if the alumina-silica ratio is kept constant and the lime content varied, the viscosity changes rather rapidly.

To make another trial of the transparent ratio scale, superimpose it on Fig. 7, plane of 15 per cent. magnesia at 1400° C. If now the field between 35 and 45 per cent. lime is examined, it will be seen that with alumina-silica ratios between $1:1\frac{1}{2}$ and $1:2\frac{1}{2}$, there is practically no difference in viscosity so long as magnesia remains constant, which it does because the plane of constant 15 per cent. magnesia was employed. This is a region in which both the alumina-silica ratio and the lime content can be varied simultaneously, and such a variation will have little effect on viscosity, of course, only within the limits indicated.

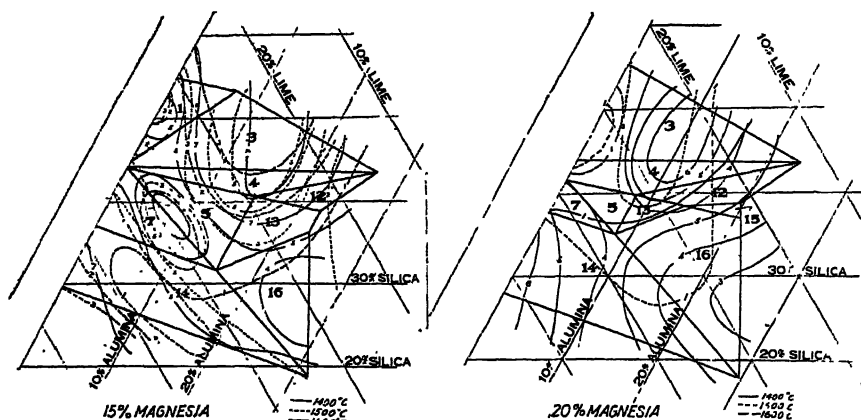
The ratio of alumina to silica in the slag is influenced most largely by the amounts of alumina and silica in the ore mixture and the lime and magnesia enter the slag most largely from the flux. When it is deter-



FIGS. 16-21.—VISCOSITY OF ANY SILICA-ALUMINA-LIME-MAGNESIA COMPOSITION, INCLUDING ALL RANGES OF BLAST-FURNACE SLAG.

mined from the viscosity diagrams that in a certain region of slag composition variations of the alumina-silica ratio have relatively little influence on viscosity, this means, of course, that the ore mixture may vary considerably in these regions with little change in the fluidity of the slag, if the lime and magnesia are kept constant. This suggests the use of certain regions of slag composition, depending on what composition ratios in the ore mixture are easy or difficult to maintain in the individual plant.

If the diagrams of viscosity at any one temperature are examined, for example, if Figs. 4 to 8 inclusive for 1400° C. are examined, beginning with 0 per cent. magnesia, it is at once apparent that slags with 5 per cent. magnesia are decidedly more fluid than those with 0 per cent. magnesia and that with increasing amounts of magnesia up to 20 per cent. the



FIGS. 22-23.—VISCOSITIES AT THREE DIFFERENT TEMPERATURES.

fluidity increases. If a similar comparison be made at 1500° C. and 1600° C., the same thing will be observed.

Not alone does composition have a very decided effect on viscosity but the effect of temperature too is decidedly marked. Figs. 19 to 23 inclusive, which are respectively on the 0, 5, 10, 15 and 20 per cent. magnesia planes but with viscosities at 1400°, 1500° and 1600° C. on each diagram, illustrate the effect of composition and temperature. By locating a particular slag composition on these diagrams, the effect of temperature change on viscosity is apparent immediately.

To illustrate the effect on viscosity of changes in composition and changes of temperature, a series of sections have been made along the various alumina-silica ratio lines beginning with 1 alumina to 1 silica and running to 1 alumina to 8 silica at temperatures of 1400°, 1500° and 1600° C. These are shown in Figs. 24 to 26 inclusive. The curves are all U's opening upward. At any one temperature the general effect of magnesia is to broaden and flatten the U. Comparing the same magnesia content

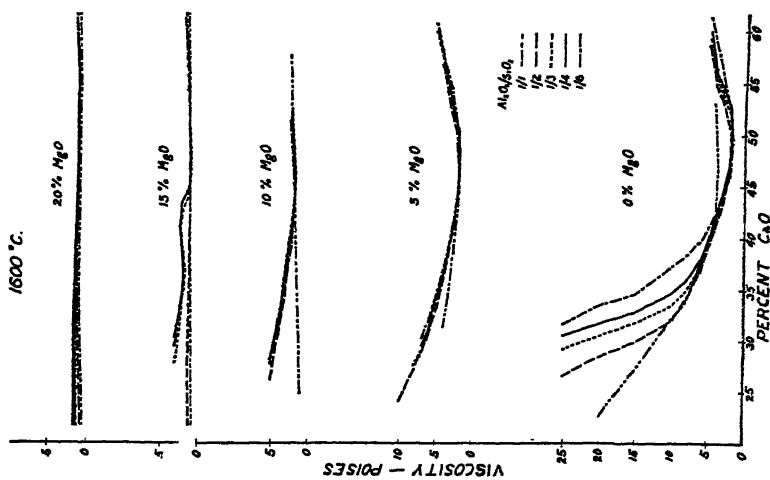


FIG. 24.

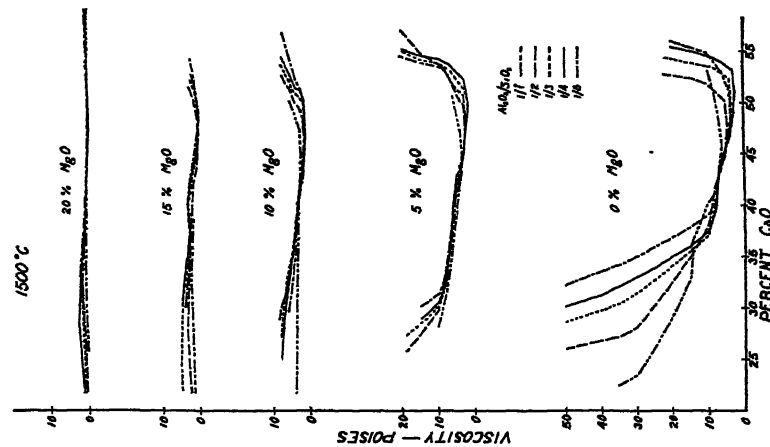


FIG. 25.

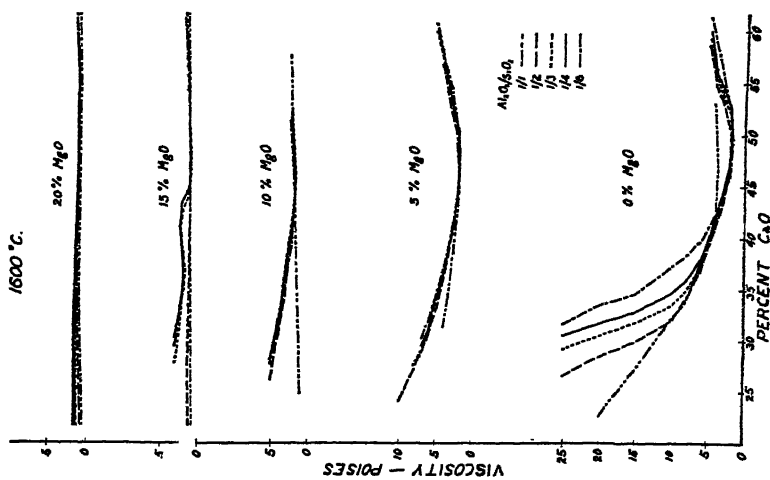


FIG. 26.

FIGS. 24-26.—EFFECT OF MAGNESIA IN INCREASING FLUIDITY.

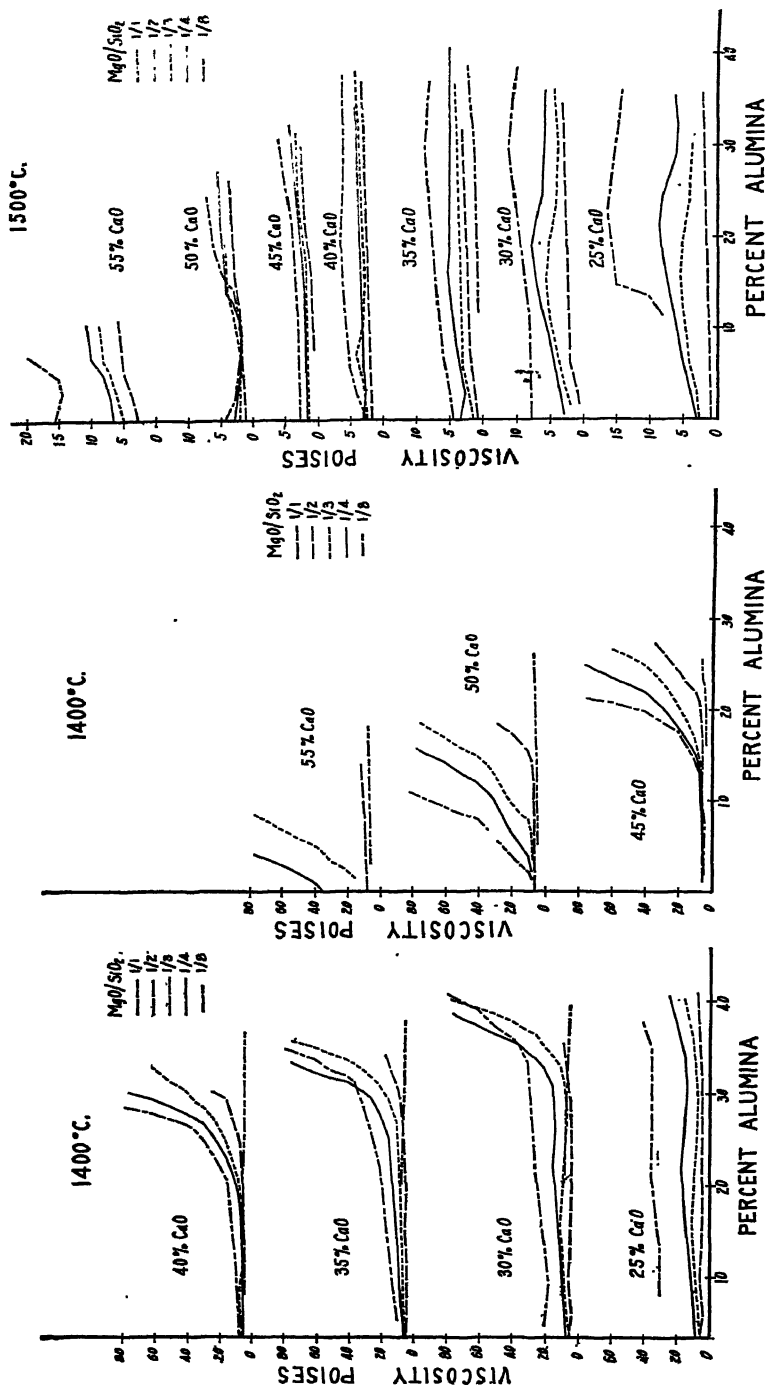
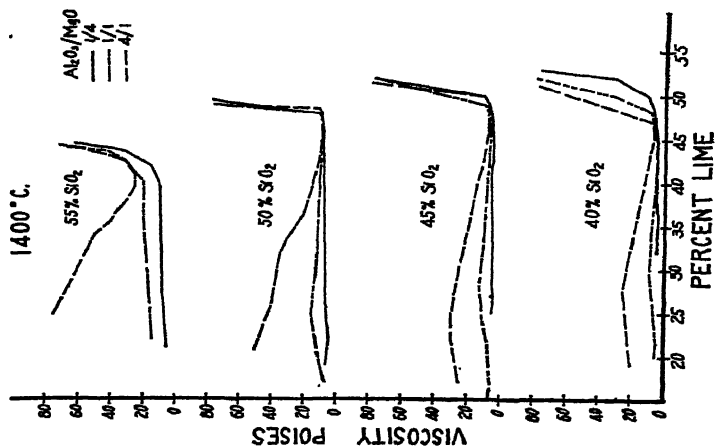
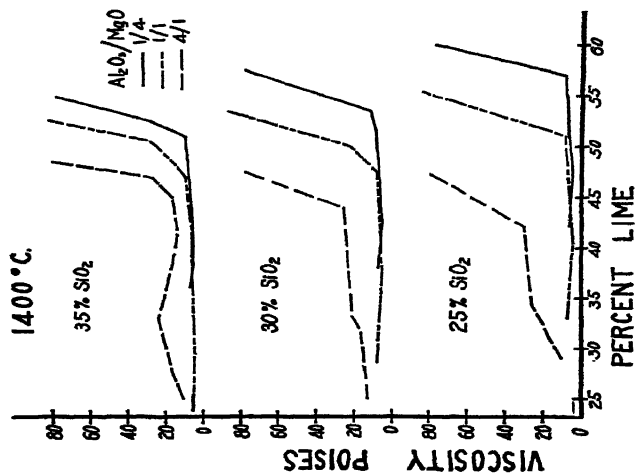
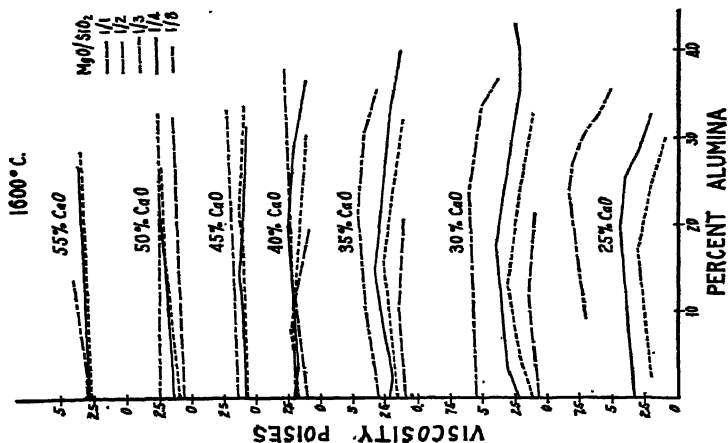


Fig. 27.

Fig. 28.

Fig. 29.

FIGS. 27-29.—EFFECT OF CONSTANT LIME AND VARYING MAGNESIA-SILICA RATIOS.



curves at different temperatures, the effect of temperature increase is the same, to broaden and flatten the curves.

These sections, Figs. 24 to 26 inclusive, make very plain the effect of magnesia in increasing fluidity. At 1400° C. (Fig. 24) with 0 per cent. magnesia, there is a range of 9 per cent. lime over which the viscosity is less than 20 poises, when the alumina-silica ratio is 1:3; and a range of 6 per cent. lime when the same ratio is less than 1:2. When 5 per cent. magnesia is present, there is a range of 14 per cent. lime over which the viscosity is less than 20 poises when the alumina-silica ratio is 1:3; and a range of 12 per cent. lime when the ratio is 1:2. When 10 per cent. magnesia is present the corresponding lime percentages for the same viscosity range become 21 per cent. for the 1:3 ratio and 18 per cent. for the 1:2 ratio. Similar figures are obtainable at the higher temperatures. This means, as was previously pointed out, that magnesia tends to reduce viscosity changes and that a furnace operating on a higher magnesia slag is operating, at least so far as viscosity is concerned, in a more regular and uniform way. This fact should be very important in its relation to desulfurization in the blast furnace.

With the many variable factors entering into the operation of a blast furnace, if one factor such as viscosity can be controlled so as to make viscosity changes of minor importance, the resulting increased uniformity of operating conditions will make more evident the effect of other variables previously obscured by the viscosity changes.

In our study we made diagrams (Figs. 14-79. See pp. 72-83) from which sections were cut illustrating the effect of magnesia. Figs. 27 to 30 are such a series of sections, each section showing constant lime and varying magnesia-silica ratios. These sections plainly show that while with low lime content the magnesia-silica ratio is important in that it does decidedly affect the viscosity, it is with the higher lime and lower alumina contents that it is most important. This effect is most clearly shown at the 1400° C. temperature in Fig. 27, and it is due probably to the increased tendency to form magnesian silicates under these conditions.

The effect of varying the alumina with respect to magnesia is shown in Figs. 31 and 32, which give a series of sections, each section being of constant silica content, while the lime and the alumina-magnesia ratio vary. The viscosities in this diagram are at 1400° C. and intermediate ratios are spaced in between those given. These sections make very apparent the necessity of running low alumina and high magnesia, especially for slags of high lime content when the silica is between 30 and 40 per cent.

In using the diagrams in this paper, it must be remembered that we have determined viscosities of silica-alumina-lime and magnesia melts and have not yet been able to investigate the quantitative effect of iron and

manganese oxide nor of the alkalies. When data regarding a particular slag are to be determined, its analysis should be refigured on the basis that the silica-alumina-lime and magnesia are equal to 100 per cent.

The illustrations by means of sections which are used in this paper were selected primarily to show the various methods of interpreting the data given in the diagram. It would be possible, of course, to make as many sections as lines could be drawn across the diagrams. When comparisons of two particular slags or of two different regions are to be made, sections along the lines of variation which it is desired to investigate should be made and compared. It is believed that all methods of comparison are illustrated in the sections but to make the greatest use of the data presented, the viscosity of the blast-furnace slag determined from the diagrams should appear on the furnace-operating reports, so that this factor is available for comparison with the others recorded. We are very strong in the belief that the daily analysis of a slag should be made on the slag sample taken from one cast and we prefer to average such analyses by pencil instead of doing it by mixing samples.

A method of analysis of the daily operating reports of a blast furnace is outlined in a paper presented at this meeting.³ All the data discussed in the paper are based on analyses of samples of slags taken at the time of a particular cast of iron. Viscosity data were not available at the time the paper was written but their inclusion would have made the results more valuable. The paper, however, indicates a method of analysis that should be worth while for the comparison of viscosity with other blast-furnace data.

DISCUSSION

[This discussion refers also to the papers beginning on pages 64 and 86.]

(*T. L. Joseph presiding*)

FOREWORD BY R. B. SOSMAN

The three papers just preceding were published under one cover in January, 1931, as *Technical Publication No. 383, Viscosity of Blast-furnace Slags*, by Richard S. McCaffery and Coworkers. The discussion of the three papers was opened by C. H. Herty, Jr., and A. L. Feild, with replies by C. H. Lorig and Professor McCaffery. This part of the discussion covered, in condensed form, essentially the same topics as had been taken up in an informal conference on slag viscosity called by Alfred D. Flinn, Director of the Engineering Foundation, on Feb. 16, 1931. Dr. John Johnston had presided at that conference and the others present were A. L. Feild, A. D. Flinn, W. H. Herschel, C. H. Herty, Jr., H. R. Lillie, C. H. Lorig, R. S. McCaffery and R. B. Sosman. It had been agreed at the conference that certain questions regarding the calibration of viscosity apparatus and the accuracy of various methods used for the measurement of slag viscosity could probably be settled satisfactorily by means of

* R. S. McCaffery and R. G. Stephenson: A Statistical Analysis of Blast-furnace Data. *Trans. A. I. M. E.* (1931) 95, Iron and Steel Div., 60.

some cooperative experimental work, and that the final publication of these three papers and the discussion thereon could profitably be postponed until this work had been completed.

All of those present at the conference were satisfied that Dr. Lillie's apparatus at the Corning Glass Works, used for measurements on the viscosity of silicate glasses in the liquid state, would give dependable values for the slags in question, because the cylindrical platinum spindle used by him is wetted by the liquid while its form eliminates any suspicion of turbulence or nonuniform flow such as can be theoretically raised against spindles of other shapes.

Accordingly, arrangements were made by which three typical slags were to be prepared and measured at the University of Wisconsin, while portions of the same slags were to be sent to the Corning Glass Works and the Bureau of Mines. Dr. W. H. Herschel of the Bureau of Standards was to receive and compare the results of the three sets of measurements.

The results were submitted in May, 1931. The final comparison, as is stated in the section on Comparative Tests, which has been added to the original paper on Determination of Viscosity (pp. 104 to 113 and Figs. 7 to 14, pp. 97 to 110), shows satisfactory agreement between the results obtained with platinum at Corning and those obtained with graphite at Wisconsin, over the entire range covered by the Corning measurements (1400° to 1550° C.). The experimental comparison, therefore, leaves no reason to doubt that the square graphite spindle used by McCaffery and coworkers gives reliable values of viscosity in the range 2 to 15 poise, and, by inference, at higher and lower viscosities also.

The viscosities obtained with the graphite apparatus at the Bureau of Mines on the same three slags deviate considerably from the two others. Unfortunately, it has not been possible to examine further into the cause of this deviation, since the Bureau of Mines withdrew early in 1931 from the research work that had been conducted jointly by the Bureau, the Carnegie Institute of Technology and the Mining and Metallurgical Boards, under which auspices the laboratory work had been conducted.

CONTRIBUTED ORAL AND WRITTEN DISCUSSION

H. R. LILLIE, Corning, N. Y. (written discussion).—Since all seem to agree that the all-platinum viscosimeter should do away with the major difficulties associated with the actual viscosity determinations and since previous work has proved that the mechanical system being used gives correct values, special attention was given to the control and measurement of the temperature in the set of comparative tests made in this laboratory, the results of which are included in Figs. 12, 13 and 14 (pp. 108 to 110).

The temperature of the main furnace windings was controlled automatically by a platinum couple installed as part of the furnace, placed close to the platinum-rhodium winding at the vertical center of the core. Auxiliary heating units and thermocouples were installed for the purpose of regulating temperature distribution.⁴

The temperature of the slag was measured in the following way: A porcelain tube covered at its lower end by a platinum foil sheath was lowered into the liquid. The couple was then inserted. After thermal equilibrium was again attained the reading was taken, the couple completely removed from the furnace and the sheathed tube raised to the upper position during the viscosity determination. Since the upper auxiliary heater prevents the conduction of heat up the sheath from the couple and since the angular opening between the two porcelain tubes is extremely small, preventing outward radiation, it can be assumed that the thermocouple reaches the exact temperature of the slag.

⁴ See *Jnl. Amer. Ceramic Soc.* (1929) **12**, 518, and *Jnl. Rheology* (1932) **3**, 124.

A new thermocouple, calibrated by the Bureau of Standards, was used for each slag and since it was not allowed to remain at high temperatures for any length of time and since the atmosphere was strictly oxidizing, I believe the calibration can be depended upon throughout the run.

F. A. HARTGEN and C. H. HERTY, JR., Pittsburgh, Pa. (written discussion).—It would appear from the results of the comparative tests by Dr. Lillie and Professor McCaffery that the square and round spindle gave almost identical results. There is still the question, however, in the plot of viscosity versus temperature for the six different spindles (Fig. 8, p. 98), where the round spindle gave entirely different results from spindles of all other shapes on the same slag in Professor McCaffery's laboratory. It is very difficult to understand how this condition could be true and yet have the square spindle of Professor McCaffery and the round spindle of Dr. Lillie check so closely. It would appear that either Professor McCaffery had unintentionally made some change in his apparatus when using a round spindle or that some other uncommon condition had entered the entire experimental work.

One statement which we cannot accept is that temperatures were measured within $\pm 5^\circ$ C. with an optical pyrometer. This degree of accuracy is possible under ideal conditions, but it has been our experience that fumes are given off by all slags at or near their melting points. Provision for removing fumes by means of a gas stream have been made in the viscosimeter built and used by the Bureau of Mines. Even though the fumes are continually removed, we do not claim a greater accuracy than $\pm 15^\circ$ C., whereas McCaffery states that no fumes are given off while his slags are in the molten condition.

A. L. FEILD, Baltimore, Md. (written discussion).—The authors are to be congratulated on the perseverance and industriousness with which they have investigated the commercially important problem of blast-furnace slag viscosity. I have unfortunately not been able to digest thoroughly the detailed data of this paper, through lack of time. I do wish, however, to draw attention to the complication which has been introduced by the use of a square spindle. This expedient does not avoid the dilemma of a possible "slip" and at the same time brings into question the calibration method as well as the absolute accuracy of the viscosity measurements.

R. H. SWEETSER, Columbus, Ohio.—Why do the authors overlook the presence of so much calcium sulfide in slag and go ahead with such highly mathematical calculations and measurements? Analyses I have had made of some blast-furnace slags showed from 4.86 to 5.16 per cent calcium sulfide.

J. JOHNSTON, Kearny, N. J.—The question under discussion narrows down to that of the calibration of the measuring device, in particular whether the ratio of the observed deflection in castor oil at ordinary temperature to that in a slag at high temperature is, or is not, the same for a square as for a round spindle. This is a question which can be settled only by appropriate comparative experiments. From the practical point of view the absolute accuracy of the results is of less importance, because the blast-furnace operator is not so much interested in the absolute viscosity of his slags as in the mode of variation of viscosity when the content of magnesia, for instance, varies. I believe that Professor McCaffery's curves and tables represent—with ample accuracy for practical purposes, at least—the variation of viscosity with composition in the four-component field which he has investigated, and hope it may be possible to extend the observations to include the influence of such other minor components as may be present in slags to an extent sufficient to influence appreciably their viscosity.

H. W. JOHNSON, Indiana Harbor, Ind.—We had to vary the Al_2O_3 in our slags and plotted Al_2O_3 contents against the average tonnages. We found that when Al_2O_3 was low, to 1.5 per cent, tonnage was lower (MgO content in these slags was about 1 per cent). The Al_2O_3 content varied from 11 to 15 per cent.

T. L. JOSEPH, Minneapolis, Minn.—How do viscosities of slags of different Al_2O_3 and different MgO contents compare?

R. S. McCaffery.—MgO decreases the viscosity.

R. H. SWEETSER.—In using oyster shells, containing no MgO, as a blast-furnace flux, it was hard to get a fluid slag to take care of the sulfur. This work of Professor McCaffery's explains the difficulties we encountered.

I. N. GOFF, Indiana Harbor, Ind. (written discussion).—These three papers present a fundamental research on the viscosity of blast-furnace slags and should be of practical value to furnace operators. The scope of the work, however, is so vast that it might be divided into a number of papers or even published in book form.

One of the salient points brought out by data and diagrams is the effect of magnesia. It is shown that variations of lime, alumina or silica, which always occur in blast-furnace slag, do not change the viscosity nearly so much when there is a high magnesia content. In addition, as the viscosity is an important factor in the desulfurizing action of the furnace, this is a valid reason for maintaining a high magnesia content in all blast-furnace slags.

The following is an excellent illustration of the practical value of the information contained in this publication. In a number of instances iron blast furnaces making standard basic pig iron began to show irregularities in operation and unexplainable decreases in tonnage when only slight burden changes had been made. The quality of the pig iron varied slightly and the only significant change in the slag composition was a drop in the alumina content from about 15 down to 10 per cent. The magnesia content of slags from these furnaces varied between 1 and 2 per cent. Fig. 2 (p. 66) of this paper not only offers an explanation for the change in operating conditions but in addition indicates two methods for bringing the furnace back to normal. The viscosity curve in Fig. 2 with varying magnesia and 10 per cent alumina at 1500°C . shows a rapid increase as the magnesia decreases below approximately 4 per cent. The same type of curve with 15 per cent alumina indicates a rather uniformly low viscosity with varying amounts of magnesia. In the case of slag analyses where the alumina content drops to as low as 10 per cent the magnesia content must be raised to above 5 per cent to obtain the desired viscosity. On the other hand, if the alumina content could be increased to approximately 15 per cent, with the magnesia present in amounts varying from 0 to about 18 per cent, the same desirable result would be obtained. In each of the cases noted it was more convenient to increase the alumina than the magnesia, so burden changes were made which increased the alumina to approximately 15 per cent and the furnaces were soon operating normally.

The value of a moderately high magnesia content could have been brought out more clearly in this paper if the data had been plotted in curves with constant magnesia and varying alumina.

In order to increase the practical value of this paper and simplify its use for furnace operation we believe significant data, diagrams, etc., should be collected in condensed form so that the information presented could be easily used for reference.

R. B. SOSMAN, Kearny, N. J.—The relation of the viscosity curves to the equilibrium diagrams of the ternary systems $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$, CaO-MgO-

SiO_2 , and $\text{CaO-MgO-Al}_2\text{O}_3$, and also of the quaternary system itself, should not be lost sight of. Many of the curves in these papers represent viscosities at temperatures where only a limited range of compositions is completely liquid. Only for this limited range of compositions can there be a true viscosity. Compositions bordering on the area of complete liquidity will be partly liquid and partly crystalline, and might be expected to behave more like a plastic than like a viscous material, although readings which could be interpreted as a viscous flow would be obtained from the apparatus, and would be of just as much practical value as the true liquid viscosities. The ternary diagrams of Figs. 14 to 79 should therefore be sharply limited on all sides, first by boundaries corresponding to the liquidus surfaces of the ternary and quaternary systems, outside of which the flow would be of different character; and, second, by another set of boundaries beyond which the material would be completely crystalline.

In several instances the viscosity curves in the paper transgress both of these boundaries. In some of these cases the probable cause of this transgression is undercooling, as is stated by the authors on p. 113. The more basic compositions, however, are difficult to undercool and they crystallize readily. It may be that in these instances the process of plotting and redrawing in order to make the results easily interpreted has led to their extrapolation into compositions which are partly or completely solid. In any event, the condition of equilibrium would seem to be the condition that should ideally be represented in the diagrams, because undercooled liquids crystallize unexpectedly and therefore it hardly seems safe to include them in a diagram which is to be put to practical use, without some indication on the diagram that they are in fact unstable.

For the four ternary systems the boundaries for complete liquidity can be drawn from the equilibrium diagrams published by the Geophysical Laboratory. In the quaternary system only a limited amount of experimental information is available, and without such information the boundaries cannot yet be completed.

This is the most extensive piece of experimental work on the viscosities of slags that has ever been presented to American metallurgists and the authors are to be congratulated upon the very satisfactory results that they have attained.

R. S. McCAFFERY (written discussion).—The last paragraph of Dr. Sosman's foreword to this discussion is the first indication we have had of the reason for Dr. Herty's withdrawal from further investigation of the viscosity of the slags used in the comparative tests that were made. We note with interest in *Cooperative Bulletin* 56, Carnegie Institute of Technology, the changes he has made in his procedure for determining viscosity including his abandonment of his calibration curve of the parabolic speed-deflection angle type.

In reply to Mr. Hartgen and Dr. Herty, we early realized that the effect of the surface tension of the slags on the spindle stem was an important factor in the determinations of their viscosities. We have pointed out in the paper (first paragraph, p. 97) that its effect would vanish if the stem of the spindle stem was infinitely small in diameter. With the straight cylindrical spindle, $\frac{1}{2}$ in. in diameter, the magnitude of the surface tension was so great as to give values considerably above the true viscosities of the materials. We tried to eliminate this effect as much as possible by increasing the size of the spindle bob, decreasing the diameter of the stem and by choosing a shape of spindle bob that would give a large torque, so that the ratio between the torque developed by the spindle bob and the torque developed by the action of surface tension on the spindle stem would be extremely large.

As we have indicated (p. 97), surface tension varies considerably, comparing one sample of slag with another of different composition and at a different temperature. Since it is impossible to eliminate entirely the small neck supporting the viscosity bob, we early realized that it was absolutely necessary to reduce the surface

tension effect to a negligible minimum and the design we have chosen accomplishes this result, as we have proved with repeated comparisons.

With respect to circular spindles or spindles of the design we adopted, there is only one question to decide, which is whether the spindle selected measures viscous flow. The criterion of viscous flow for an apparatus of the type we employed is that the angular deflection shall be proportional to the speed of rotation. This can be readily seen from inspection of the formula

$$\eta \text{ (Poises)} = \frac{K\phi}{S}$$

There is nothing mysterious about it whatever and we have shown in Fig. 11 (p. 106) a type diagram illustrating this straight-line relationship. The speed of rotation-deflection angle diagram cannot be anything else than a straight line—it cannot be a parabola or other curve and still satisfy the relationship expressed in the formula for viscous flow.

The accuracy of our temperature results was checked repeatedly with melting points established by the Bureau of Standards and we are positive our results are correct within the limit of accuracy stated in our paper.

If Dr. Herty says fumes were given off in his furnace by the slags he prepared, I am quite willing to agree that his observations of his work are correct. We have said that our furnace was free from fumes during a viscosity determination. This is not only the observation of the writer of this reply, but also the observation of every one of the six men who have worked with our apparatus.

Mr. Feild's criticism is fully answered on pp. 104 to 113 of our paper. We regret as much as Mr. Sweetser does our lack of data on the effect of calcium sulfide in slags but we had to make a beginning in our work, which we did by using synthetic slags of four components. We hope we may be able to continue our work to include calcium sulfide as well as iron and manganese oxides and the alkalies.

In answer to Dr. Johnston's question as to whether the observed deflection in castor oil at ordinary temperatures can be compared with a slag at high temperatures, it happens that this no longer is part of the problem for Dr. Lillie has calibrated his apparatus in absolute units (reference 25, p. 121). Our work closely checks Dr. Lillie's determination on slag samples we sent him, so our results are in absolute viscosity units.

We highly appreciate the comment of Mr. H. W. Johnson and Dr. I. N. Goff as illustrating the practical application of our data.

We entirely agree with Dr. Sosman's discussion on the limits of complete liquidity in the systems investigated and we realize that much additional work remains to be done. However, we observed in our work that supercooling of slags is very prevalent. Whenever we obtained data in the supercooled region we published the results, in spite of the fact that the condition is one of metastability, because we believed the slags in blast furnaces probably supercooled as did our experimental slags and that our results might be of some benefit to blast-furnace operators.

We desire to express our deep appreciation of the courtesy of Dr. Lillie and of the officials of the Corning Glass Co. for the assistance Dr. Lillie has given us in checking our results in his viscosity apparatus.

Some Effects of Temperature and Iron Oxide in the Manufacture of Basic Open-hearth Steel

By W. J. REAGAN,* OAKMONT, PA.

(New York Meeting, February, 1932)

MANY factors enter into the manufacture of basic open-hearth steel of high quality. Perhaps the two most important are temperature and the iron oxide content of the metal. If we can control these two factors we can essentially control basic open-hearth practice.

SOURCE AND EFFECT OF IRON OXIDE

Earlier investigators, especially Herty and his associates, have shown that iron oxide is introduced into the open-hearth furnace in four ways:¹

1. By oxidation of the scrap by furnace gases.
2. By decomposition of the limestone.
3. By oxidation of the iron oxide in the slag by furnace gases.
4. By direct addition of iron ore to the charge.

We also know that the speed of operation of an open-hearth furnace depends, for a given charge and given combustion conditions, on the rate at which iron oxide will diffuse from the slag into the metal. The rate of diffusion depends upon a number of variables, such as iron oxide content of the slag, slag viscosity, etc., which also depend upon the amount of iron oxide in the metal, amount of carbon present, temperature, and so forth.

For a given carbon and a given temperature, the iron oxide content of the metal is in proportion to the iron oxide content of the slag. This fact can be easily verified by analysis of slag samples taken as described by Herty.² It is preferable to take these samples just before deoxidation. In killing the steel samples with aluminum it is desirable to use aluminum rod of 99 per cent purity; ordinary commercial aluminum rod with a purity of approximately 92 per cent is not satisfactory. In drilling these samples it is also essential to take the largest amount of drillings possible. This gives more accurate results because it eliminates spotty segregation of Al_2O_3 .

* Open Hearth Dept., Edgewater Steel Co.

¹ Solubility of Iron Oxide in Iron. Carnegie Inst. of Tech. *Bull.* 34.

² C. H. Herty, Jr., J. M. Gaines, Jr., H. Freeman and M. W. Lightner: A New Method for Determining Iron Oxide in Liquid Steel. *Trans. A. I. M. E., Iron and Steel Div.* (1930) 28.

Fig. 1 shows clearly how the amount of iron oxide in the steel is in proportion to the amount of iron oxide in the slag. In determining the total iron oxide in the slag, the figures used are FeO plus 1.35 times Fe_2O_3 . These figures give total FeO based on molecular concentration in the slag. They are for high-carbon steel (0.60 to 0.80 per cent C), all bottom cast, with temperatures considerably higher than top-cast steel.

FACTORS DETERMINING AMOUNT OF IRON OXIDE IN FURNACE BATH AT MELTING

In an effort to ascertain the importance of various factors influencing the iron oxide content of the bath at melting, a great many heats were

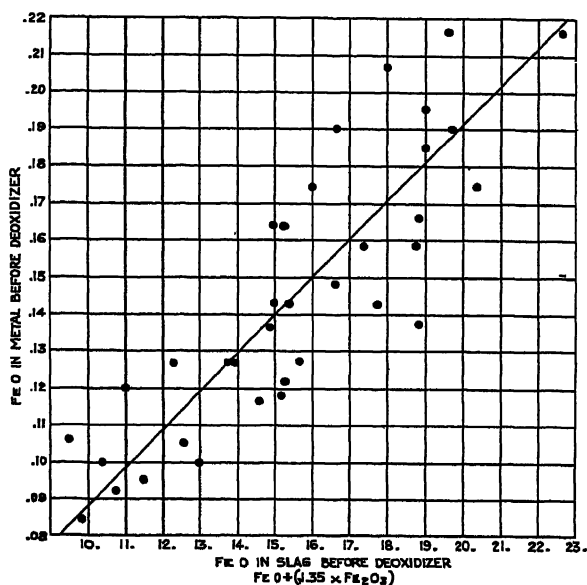


FIG. 1.—RELATION OF IRON OXIDE IN STEEL TO IRON OXIDE IN SLAG.

examined for all possible causes. In a very large proportion of the heats studied, one factor appeared to be of much more importance than any of the others. This factor is clearly shown in Fig. 2. The plotted chart shows a pronounced tendency toward lower iron oxide content, the more quickly a heat is melted and under bath. While fast melting seems to have the greatest influence, the longer refining period to free the bath of all iron ore contamination seems also of considerable importance.

One other factor, which cannot be charted in any way, and which probably reflects indirectly upon the figures given above, is atmosphere control. This might be more accurately described as "flame control." This factor can be quickly checked by replacing a competent furnace operator by a man unfamiliar with furnace operation, or one not accus-

tomed to watching his flame carefully. The quickest way of comparing results of these two operators is an examination of the residual manganese content of the steel just before deoxidation. As a rule, it will be found that the experienced operator will carry a noticeably higher residual manganese, which is due to a lower iron oxide content of slag and metal. It is assumed, of course, that the heats to be compared have a charge of approximately the same pig and scrap content, assuring an equivalent amount of manganese in the charge in the heats to be compared. It is also assumed that metal temperatures are approximately the same in each case.

This factor controlling residual manganese is nothing more than oxidation, which is of very great importance in the control of iron oxide. A cold working furnace is a contributory cause to this condition (over-oxidation) and is probably more noticeable in a furnace fired with producer gas than in one using any other type of fuel. This is probably due to the natural clogging up of the regenerators in a furnace using producer gas and to the tendency of the operator to "push" the furnace to make up for its sluggishness due to old age.

EFFECT OF IRON OXIDE AND TEMPERATURE ON RESIDUAL MANGANESE

In a study of the effect of iron oxide on the various constituents of open-hearth steel, perhaps the most noticeable fact is its influence upon residual manganese. Temperature helps to make this effect most noticeable.

As the percentage of iron oxide in the metal (which is in proportion to the iron oxide content of the slag) decreases, and as the temperature of the steel increases, so also does the residual manganese increase. These factors follow one another so closely that, for a given charge, assuming temperatures to be within a consistent range, the iron oxide content of the slag, or metal, can be determined by the manganese content of the bath. In steel of 0.60 to 0.80 carbon content, where the proper precautions are taken to insure that iron oxide is at a minimum, a residual manganese of 0.50 to 0.55 per cent denotes an iron oxide content in the slag of about 10 per cent. A residual manganese of 0.30 or 0.35 per cent denotes an iron oxide content of approximately 15 to 16 per cent.

The effect of low iron oxide and low temperature are clearly shown in Fig. 3. In comparing numerous slag samples, which all contained approximately the same percentage of iron oxide, with the residual manganese content of the steel at the time the slag samples were taken, it will almost invariably be apparent that for a given iron oxide content in the slag the higher residual manganese will always show a higher temperature. In making these comparisons it is well to keep in mind the fact that heats to be compared must have the raw material charge as near alike as possible.

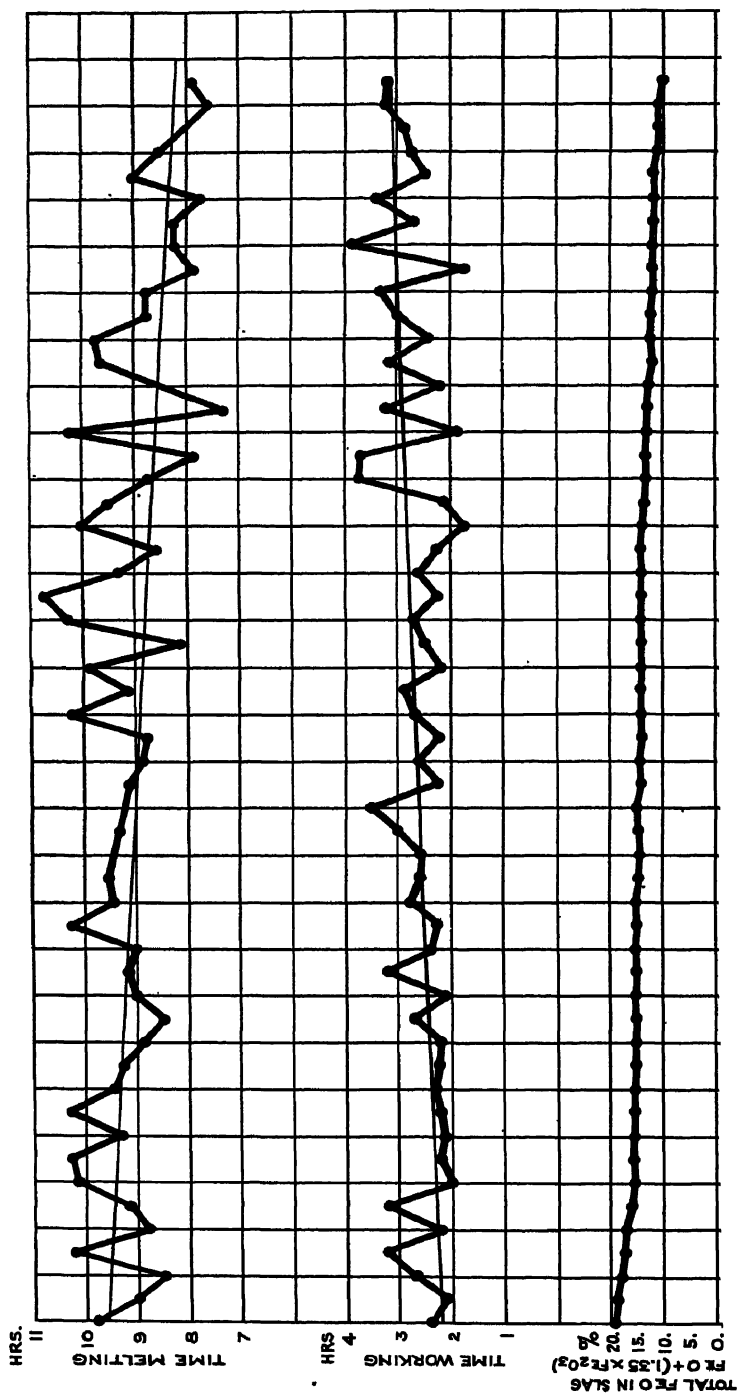


Fig. 2a.—CAPTION ON OPPOSITE PAGE.

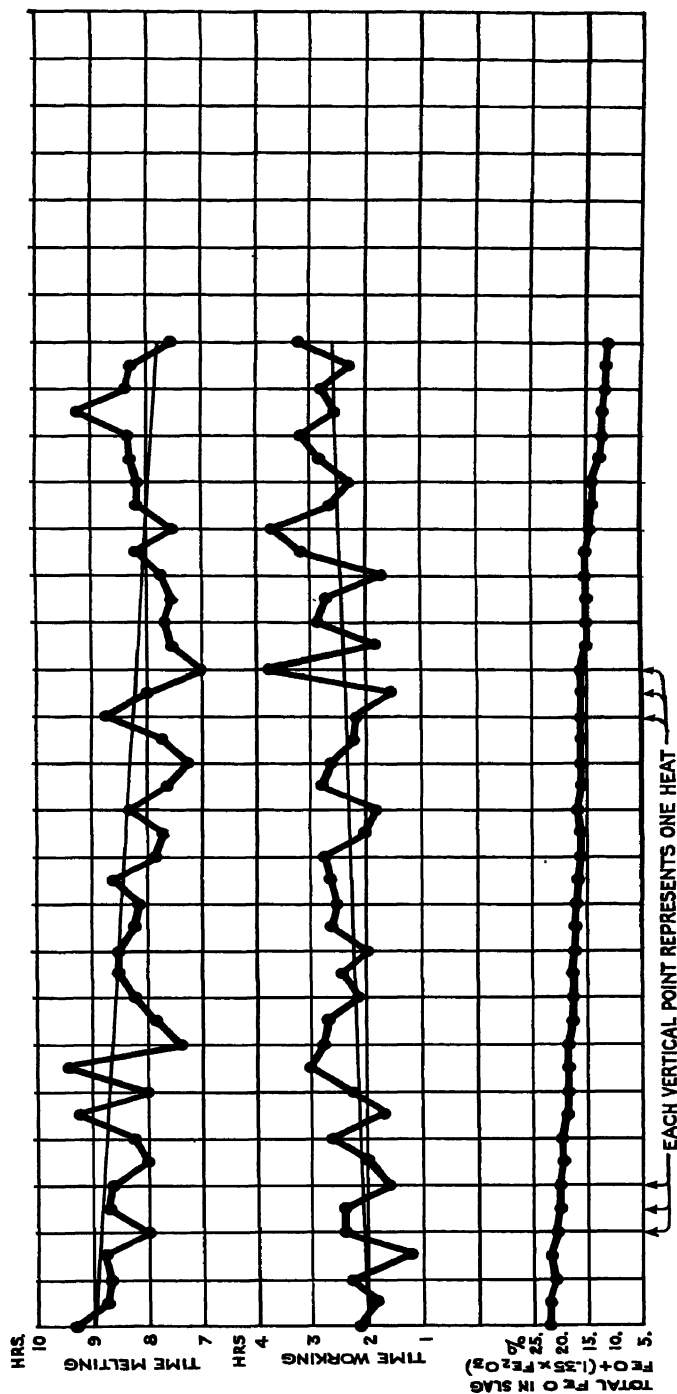


Fig. 2b.

FIG. 2.—RELATION OF IRON OXIDE CONTENT TO SPEED OF MELTING.

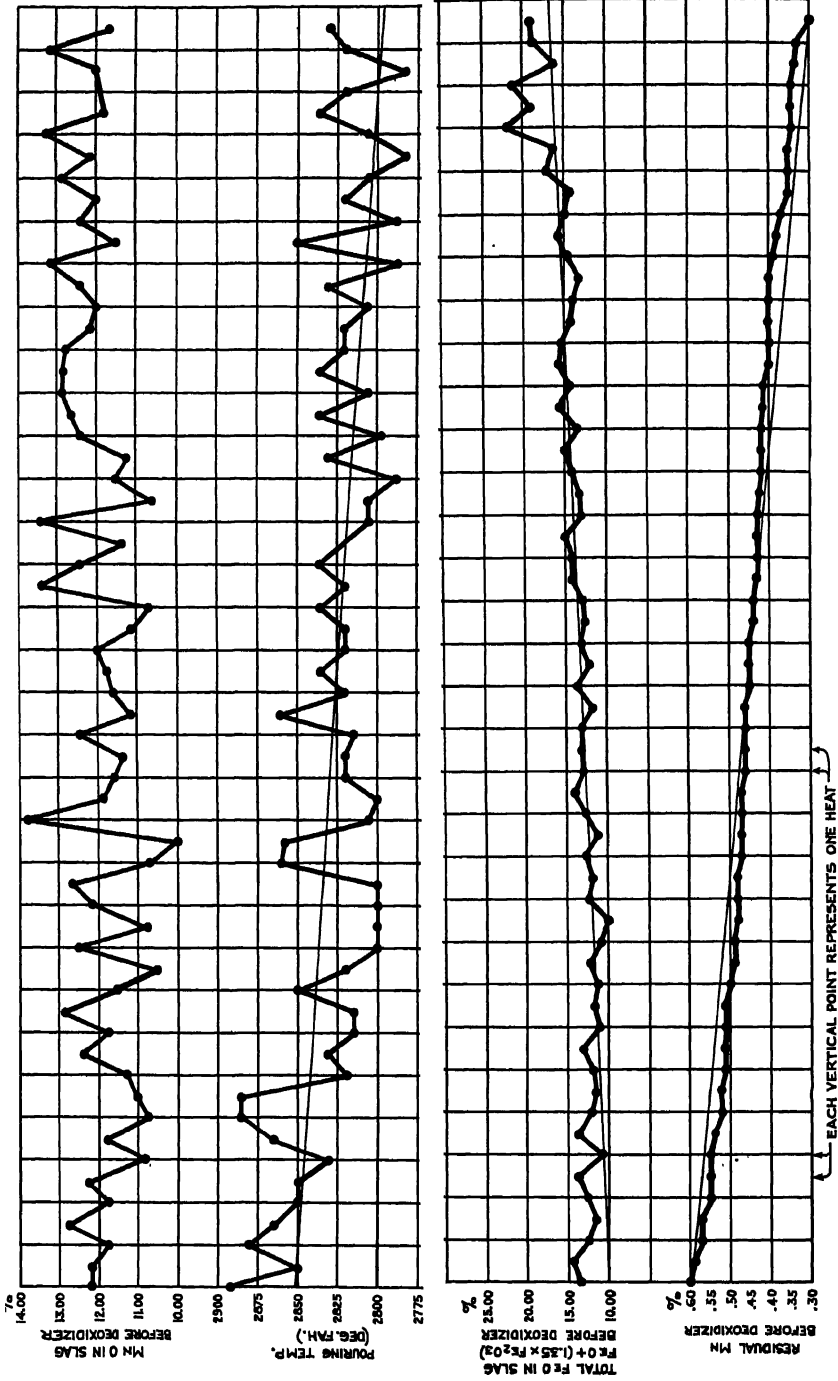


FIG. 3 — EFFECT OF LOW IRON OXIDE AND LOW TEMPERATURE.

Other constituents of the slag also have considerable effect upon its iron oxide content. The most noticeable factor is SiO_2 . Fig. 4 shows that low iron oxide is nearly always followed by high SiO_2 . Apparently the most desirable combination is to have the SiO_2 as high as is consistent with basic open-hearth operation, which probably depends upon the

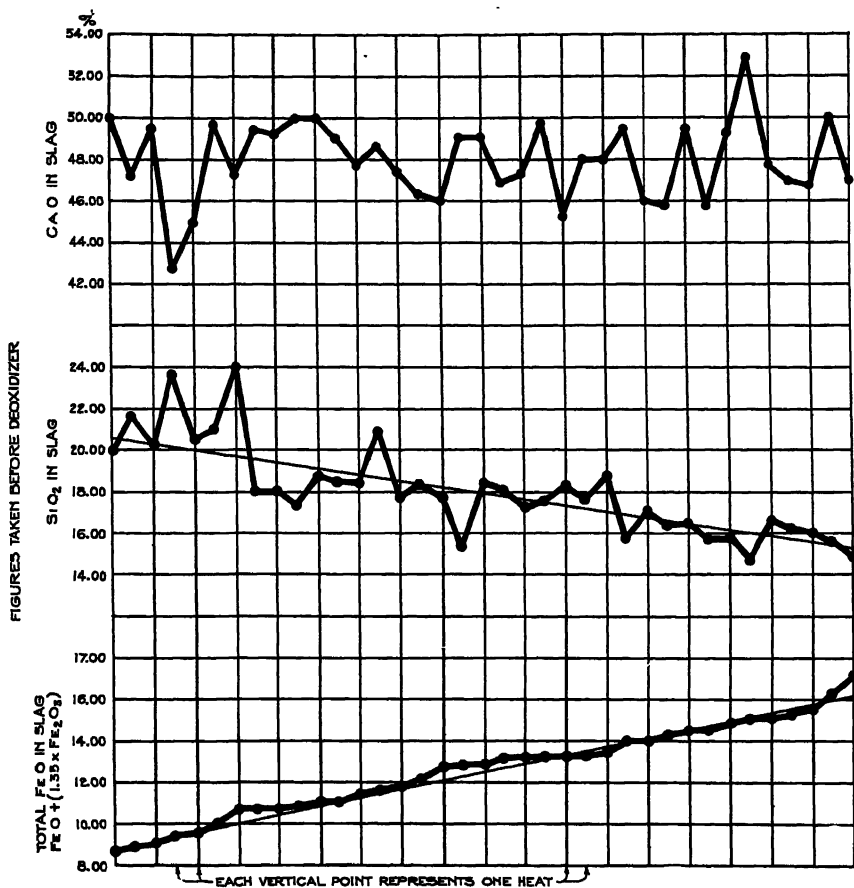


FIG. 4.—RELATION OF IRON OXIDE TO SiO_2 .

phosphorus content of the steel being manufactured. What causes this combination of high SiO_2 and low FeO is not quite fully understood. The lime charge, no doubt, is partly responsible for the result, but other factors, possibly slag volume, are equally important. It is hoped that later figures may be available showing how to arrive at this happy combination consistently.

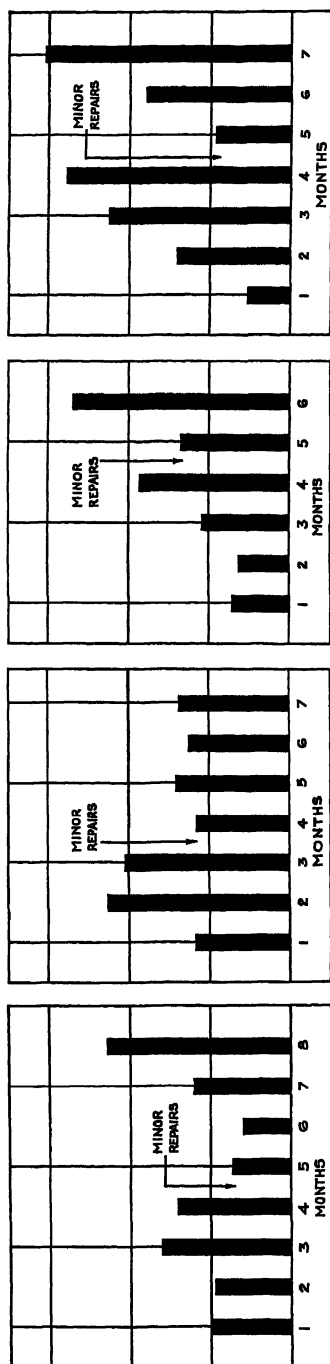


FIG. 5.—EFFECT OF FURNACE LIFE ON OPEN-HEARTH REJECTIONS.

Each group represents one complete furnace run from time furnace is started until it is shut down for general repairs. Each vertical block represents all open-hearth rejections chargeable to steel produced during that month's production of approximately fifty 90-ton heats.

EFFECT OF FURNACE LIFE UPON OPEN-HEARTH REJECTIONS

Furnace temperatures depend largely upon furnace life. The effect of furnace life upon temperature, and correspondingly upon open-hearth rejections, is a most important one, and not generally known. This effect can be closely followed in Fig. 5. The resemblance of the curves, of the four individual furnace runs, one to another, is most striking. It shows vividly that when furnace temperatures are normal, or above, open-hearth rejections are low, and that as the furnace grows older, and temperatures accordingly decrease, the rejections naturally increase. These figures were obtained by charting all of the scrap from each heat for four complete furnace runs and is based on approximately 100,000 tons of steel. The work of assigning each rejection to its proper heat is accomplished by the use of an automatic tabulating machine, without which the work would have been almost impossible.

It is extremely difficult to chart in any way the effect of iron oxide on open-hearth rejections, but it can be said that such rejections are almost in direct proportion to the degree of deoxidation to which the bath is brought before tapping. The Bureau of Mines investigators have shown that the use of manganese-silicon alloys of the proper proportion have the property of deoxidizing steel more thoroughly than any alloys investigated. It can be said here that the use of

these alloys in our practice has reduced open-hearth rejections to a figure never before obtained, and possibly never expected.

CONCLUSIONS

1. The percentage of iron oxide in the metal is in proportion to the iron oxide content of the slag.

2. The amount of iron oxide in the metal, which for a given carbon, and given temperature, is in proportion to the iron oxide content of the slag, can be controlled by proper melting and working conditions. Fast melting and slow working or refining keeps the iron oxide at a minimum.

3. The percentage of iron oxide in the slag, and in the metal, plus the temperature, determines the percentage of residual manganese in the steel. Low iron oxide and high temperature mean a saving in final manganese additions to the open-hearth furnace.

4. Furnace life or, in other words, furnace temperatures, govern the percentage of open-hearth rejections. Automatic furnace control that will actually control furnace atmosphere, and also combustion conditions, will be a long step towards control of iron oxide and open-hearth rejections.

DISCUSSION

(*F. M. Becket presiding*)

R. S. DEAN, Washington, D. C. (written discussion*).—Mr. Reagan has presented interesting data on steel melting practice. According to his figures the iron oxide in the bath may vary 50 per cent with constant iron oxide in the slag. This seems rather a large variation to cover by the term "proportionality," and I wonder if this lack of proportionality should not be given greater emphasis. The observation that high SiO_2 and low FeO in the slag may be obtained is important, and I would like to make some suggestions as to how this desirable condition might be obtained. High silica and low iron oxide evidently result from the preponderance of the reaction $\text{FeO} + \text{Si} \rightarrow \text{Fe} + \text{SiO}_2$. Hence, if the heat can be so controlled as to favor this reaction over those of the slag with MnO and C , the desired result will be obtained. In lead softening, which is an analogous operation to open-hearth refining, it has been found that the higher oxides of antimony may act as oxygen carriers; and we may postulate that the oxidation of manganese and carbon takes place in considerable measure by reaction with the Fe_2O_3 content of the slag, while Si is oxidized by FeO . Keeping the slag reduced—that is, free from Fe_2O_3 —should therefore enable the silicon to be oxidized preferentially. It is unfortunate that Mr. Reagan's results should all be reported as $\text{FeO} + 1.35 \times \text{Fe}_2\text{O}_3$. A determination of the magnetite content of the slag might yield important information. This could probably be done best by means of the magnetic balance. This method is being used with considerable success by the Bureau of Mines for the determination of magnetite in copper slags, and if the slags used were available some determinations could no doubt be made at the Tucson station.

R. B. SOSMAN, Kearny, N. J.—Mr. Dean is right in suspecting that the percentage of iron oxide in the metal is not proportional to that in the slag. This is true because

* Published by permission of the Director, U. S. Bureau of Mines.

the iron is present in the slag in more than one form, and there is a varying equilibrium within the slag as well as between slag and metal. The slag has usually been treated theoretically as a homogeneous phase, but actually it is not. In the open-hearth furnace the slag often contains solid phases which either carry some iron oxide or by their presence make the iron more concentrated in the liquid phase than the analysis shows. The iron oxide in the solid phases is practically removed from activity with respect to the bath. Magnesia, for instance, may be present in the suspended solid state and may take out of the open-hearth slag quite a large proportion of its oxide. Naturally, that would diminish the proportion in the metal. Professor McCaughey discussed this effect of magnesia, in the Institute's Open-Hearth Conference No. 12 (1930), and was, I believe, the first to point out its importance.

C. E. SIMS, Indiana Harbor, Ind.—Maintaining a low iron oxide content in the slag is a means of saving manganese in the open-hearth furnace. We have conducted experiments which verify the observations of Mr. Reagan. Moreover, we have found that there is an increase in the manganese content of the bath under certain conditions of low oxide content in the slag, but under these conditions there is grave danger of low ductility in the steel if the carbon content of the steel is on the high side.

A. B. KINZEL, New York, N. Y. (written discussion).—In addition to certain other phases of the problem, it should be noted that Mr. Reagan's data particularly affect our conception of the order of some of the constants used in theoretical considerations of the reactions. The equilibrium constant for the iron oxide-carbon reaction as determined in the open hearth is given as 0.01. Determined in the laboratory under supposedly ideal theoretical conditions, a value of 0.0005 resulted. It is evident that if the amount of oxygen in steel in the open-hearth furnace is a function of the oxide content of the slag, whether it be a direct function or one which must be modified by the presence of MgO , the equilibrium of the iron oxide-carbon reaction is never even approached, and the figure as obtained in the open hearth is a working solubility product under certain conditions, but must be much too high for the equilibrium constant. This tends to indicate that 0.0005 may well be of the correct order of magnitude.

J. H. FLAHERTY, Aliquippa, Pa. (written discussion).—Mr. Reagan's excellent paper contributes confirmatory data as to the working out in practical operations of slag-metal reactions in an open-hearth furnace. This is accomplished in such a concise style that in these days of voluminous technical literature it may well serve as a model.

The scatter of the points for both time working and time melting in Fig. 2 prompts the thought that other factors are far more influential than furnace time in determining iron oxide content. The trend is, however, sufficiently positive to justify Mr. Reagan's conclusion that fast melting and slow working tend to minimize iron oxide content.

The relationship of SiO_2 to FeO content in the slag and the author's comments as to the desirability of maintaining the proper combination of these are interesting. We understand that this feature has already had attention by practical operators, and that it is now the practice in some plants to add SiO_2 and burnt lime to control volume and basicity of the slag. This serves to reduce FeO , thus tending to increase Fe yield of the furnace and improve the quality of the product.

From the fact that the author was able to show directly the influence of furnace conditions on steel rejections, and was unable to show a similar direct relationship for iron oxide content, one might assume that for the conditions given pouring temperatures were a larger factor, which completely masked any minor influence the iron oxide content may have had on steel quality.

The inference that higher pouring temperatures beget lower steel rejections, while applicable for bottom pouring, hardly holds for top pouring. High temperatures and sharp working are desirable for the melting and refining stages, but teeming temperatures should be as low as practicable for top pouring. High temperatures for top pouring would ordinarily result in greater losses due to segregation of metalloids and nonmetallics, pipe cavity, ingot cracks, seams, etc.

The application of the automatic tabulating machine to the correlation of data is interesting, and we believe points out an avenue whereby all producers could profitably develop their steelmaking practices. In all steel mills numerous scattered data are available, but the mechanical task of collection and correlation of these data is so great that little of such correlation is attempted. The tabulating mechanism referred to would seem to offer a practicable tool for such work.

L. F. REINARTZ, Middletown, Ohio (written discussion).—After 15 years of experience in the control of open-hearth quality by slag analyses, I must say that in order to have a proper control many factors must be taken into consideration, such as temperature of the bath, type of fuel, analyses of the charge, especially with reference to silicon content, percentage of flux, age of the furnace, type of scrap—light or heavy—and so forth. Unless these factors are known and their effect calculated, slag volumes are likely to vary, and it will be almost impossible to compare one heat with another. It is true, if these factors are properly evaluated and the carbon content of the bath and the temperature of the bath are known, we can be fairly certain that the iron oxide of the metal is in proportion to the iron oxide in the slag; and that conclusion, as to quantity of deoxidizers needed, may be drawn from such slag analyses.

It has been our experience that heats which are melted rapidly will contain less iron oxide than those made in a sluggish furnace. Mere length of time of refining is not a sure sign that the iron content of a bath will be low. It may, in low-carbon steels, be just the opposite. The refining period should be only long enough to meet the required analysis and work all free ore out of the slag and metal bath before tapping.

In our experience, the type of fuel and character of the flame, as well as the presence of excess oxygen for combustion, has a vital bearing on the iron oxide in the slag and metal. Often the furnace design and maintenance is such that proper atmosphere is beyond the control of an ordinary first helper. It is true that if the type of flame can be controlled, the residual manganese will be higher in a bath if the flame has been kept as nearly neutral as possible. It has also been our experience that the residual manganese in a high-carbon heat will be higher if the temperature of the bath is kept well above the melting point of the steel. This is not true of small traces of manganese, however, in low-carbon steels.

Furnaces operated with natural gas or fuel oil as a fuel are more subject to fluctuations in iron oxide content of the slag and bath than when producer gas is used. The latter, if a properly designed and operated furnace is available, will give the lowest rate of oxidation of any fuel known due to the type of flame which guarantees complete bath coverage.

When a producer gas furnace becomes clogged up so that "forcing the furnace" is required it is economy to shut it down at once and rebuild it.

Mr. Reagan's charts show in a graphic manner how the iron oxide in the slag decreases with increased speed of melting. The curve showing how the iron oxide decreases with prolonged working of a heat is not quite so conclusive.

To my mind, one of the most potent factors in controlling the iron oxide content of a slag or bath is the silicon content of the charge. It is perfectly possible to control iron oxide in the slag by a proper consideration of this factor. Theoretically, perhaps, it would be advisable, in order to reduce the percentage of flux, to keep the silicon content of the pig iron, for example, very low. We know, however, from sad experi-

ence that low-silicon iron, say containing 0.60 to 0.80 per cent Si, is often made in a physically cold hearth and all kinds of quality difficulties may come from such pig iron. We know, on the other hand, that in the manufacture of medium carbon grades of steel, a silicon content of 1.00 to 1.20 per cent in the pig iron will produce a rapidly melting charge and one of which the temperature will be high enough so that ore can be worked through the bath in a minimum refining period. Furthermore, scrap containing no silicon is likely to be overoxidized in melting and cause high iron oxide in the slag and metal. We realize, of course, that the plant manufacturing high-carbon steels may be overburdened with such scrap. This means that particular care must be exercised in the manufacture of pig iron for such a practice, so that it will be of the proper quality if low silicon content is desired. The higher silicon charge lowers the iron oxide content of the metal simply because during the melting period, while it is being burned out, the metal is protected from excessive oxidation. In low-carbon steel, especially "rimming" steel, the open-hearth operator's job is so to balance the silicon content of the charge with the percentage of flux and the temperature of the bath that the ideal iron oxide content of the slag will be obtained. A low iron oxide in the slag of a "rimming" steel is a detriment to good rimming action. It is, at times, necessary to add fine iron ore, scale, or spar to such a slag to increase the iron oxide content to make the slag fluid enough to allow the free escape of gases from the bath. Conversely, it is true that the iron oxide may be so high that excessive amounts of deoxidizers are needed, and "wild" heats may result with attendant poor quality of product.

As I have said before, the final bath temperature depends not only on the condition of the furnace—whether sharp or sluggish—but also on the percentage of flux and the silicon content of the charge. Mr. Reagan's curves, showing the effect of furnace life on the rejections in the manufacture of high-carbon steels, are enlightening and suggest that others might check their practice by following their heats through to the inspection table with this in mind. Some classes of production will lend themselves more readily to such an analysis than others, depending on the number of operations from ingot to finished product. In the manufacture of sheets, for instance, the operations are so numerous before the metal in the ingot form is inspected as a sheet that it is very difficult to trace open-hearth defects through to the finished product.

I believe that the use of a manganese-silicon alloy is a decided step forward in the deoxidation of a bath before tapping. I agree with Mr. Reagan's conclusions, and believe his paper will give food for thought to steel plant operators and metallurgists.

W. J. REAGAN (written discussion).—In regard to Mr. Dean's remarks, the figures given no doubt show a rather large variation. If he will keep in mind the fact that each point represents one 80-ton heat of steel, and the figures given were obtained under operating conditions, we believe he will look more kindly on our claim that the iron oxide in the metal is in proportion to the iron oxide in the slag. Under actual operating conditions it is an impossibility to have all factors, such as temperature, melting conditions, oxidation of the slag and metal, make up of the charge, etc., remain constant. The curve shown was obtained from actual operating conditions, and this trend has been shown in the work of numerous investigators of open-hearth slags and metal, in laboratory studies. We feel that the chart depicts the ratio of slag to metal very well, and in the light of our present knowledge believe that the iron oxide in the metal is in proportion to the iron oxide in the slag. Mr. Dean's comments on the reactions involved are interesting, and his suggestions as to the magnetite content of the slag bring up a point that we have investigated very little. It is our intention to look further into the possibility of magnetite in our slags.

It seems to me that a study of the basic open-hearth slag problem is one that the U.S. Bureau of Mines is far better equipped to handle than any other agency. It is to be hoped that their future investigations will include a study of open-hearth slags.

We are familiar with Professor McCaughey's study of the effect of magnesia in open-hearth slags, mentioned by Dr. Sosman, nevertheless from our present knowledge of open-hearth slags, we feel that our claim that the iron oxide in the metal is in proportion to the iron oxide in the slag is reasonably correct. At least it answers many questions that arise in practical open-hearth operation. We realize that we have much to learn about open-hearth slags, and it is to be hoped that our lack of knowledge will be reduced considerably in the near future.

I wonder if Mr. Sims has noted temperatures whenever he has obtained low iron oxide in the slag, and an increase in the manganese content of the bath. For a given iron oxide the manganese increases with temperature. We have been able to follow this condition very closely. Low ductility of the steel has not been a problem with us.

I am sorry that I can give Mr. Kinzel no information other than that in the paper in regard to the iron oxide-carbon equilibrium reaction.

Replying to Mr. Flaherty, while furnace conditions many times serve to mask any effect of iron oxide on steel quality, we have found conditions where the effect from iron oxide can well be noted and at times this condition is of very great importance, resulting in extremely high percentages of rejections.

We are glad to have Mr. Reinartz's word that many of our findings have been found to be true by other operators. In trying to control open-hearth operation by slag control we understand the magnitude of the work. We have endeavored to maintain as constant as practically possible our raw-material charge, temperatures, flux charge, flame control, etc. We believe that such control has been profitable, even though many items are subject to considerable variation. One factor mentioned by Mr. Reinartz, silicon content of the charge, has a tremendous influence. We also know from past experience the disadvantages of low-silicon iron in the charge. Pig with a silicon content of about 1.00 per cent has given us best results. We agree with Mr. Reinartz's remarks on furnaces operated by producer gas. Apparently they give the lowest oxidation of any known fuel. Whether their higher cost of maintenance is offset by the lower iron oxide is another problem.

Inclusions—Their Effect, Solubility and Control in Cast Steel

By C. E. SIMS* AND G. A. LILLIEQVIST,* INDIANA HARBOR, IND.

(New York Meeting, February, 1932)

THE following presentation is more a summation of observations made and conclusions drawn over a period of three to four years than a report of experiments made with a definite objective. Tests were made, of course, to verify hypotheses, but the large mass of data was collected incidental to other work. Lack of space forbids the presentation of more than a few of those data. On the other hand, it is unfortunate that some of the most illustrative examples are not available. The work is admittedly incomplete but is presented in the hope that it will stimulate further work along a similar line. The answers to many of the questions left unanswered by this paper will be found only after long and painstaking study, such as is scarcely possible in a commercial laboratory where problems of immediate importance consume most of the time. It is also hoped that this study will in some measure throw light on some of the dark spots of steelmaking, and help to clarify some of the annoyingly vague references to "good practice."

Only cast steel was studied and the conclusions apply to cast steel, but it is the authors' opinion that the quality of rolled or forged steel is largely dependent on the quality of the ingot, which is a casting.

Although this discussion deals almost entirely with inclusions, it is important that the reader understand that only those natural inclusions which owe their origin to the solubility of certain materials in steel and to the chemical reactions of steelmaking are considered. Accidental inclusions, such as entrapped particles of slag, nozzle, runner, or mold are outside its province and are not considered. Such accidental inclusions are always dangerous and should be carefully avoided.

RELATION BETWEEN DUCTILITY AND NONMETALLIC INCLUSIONS

In September, 1928, an acid electric furnace was put into operation at the Indiana Harbor plant of the American Steel Foundries. Following the usual practice, aluminum additions were made in order to obtain sound castings. Immediately the problem of low ductility arose. Previous to that time, only open-hearth steel was produced, and, aluminum being used rarely in that steel, there had been practically no trouble with low ductility in the lower carbon range.

* Research Metallurgist, American Steel Foundries.

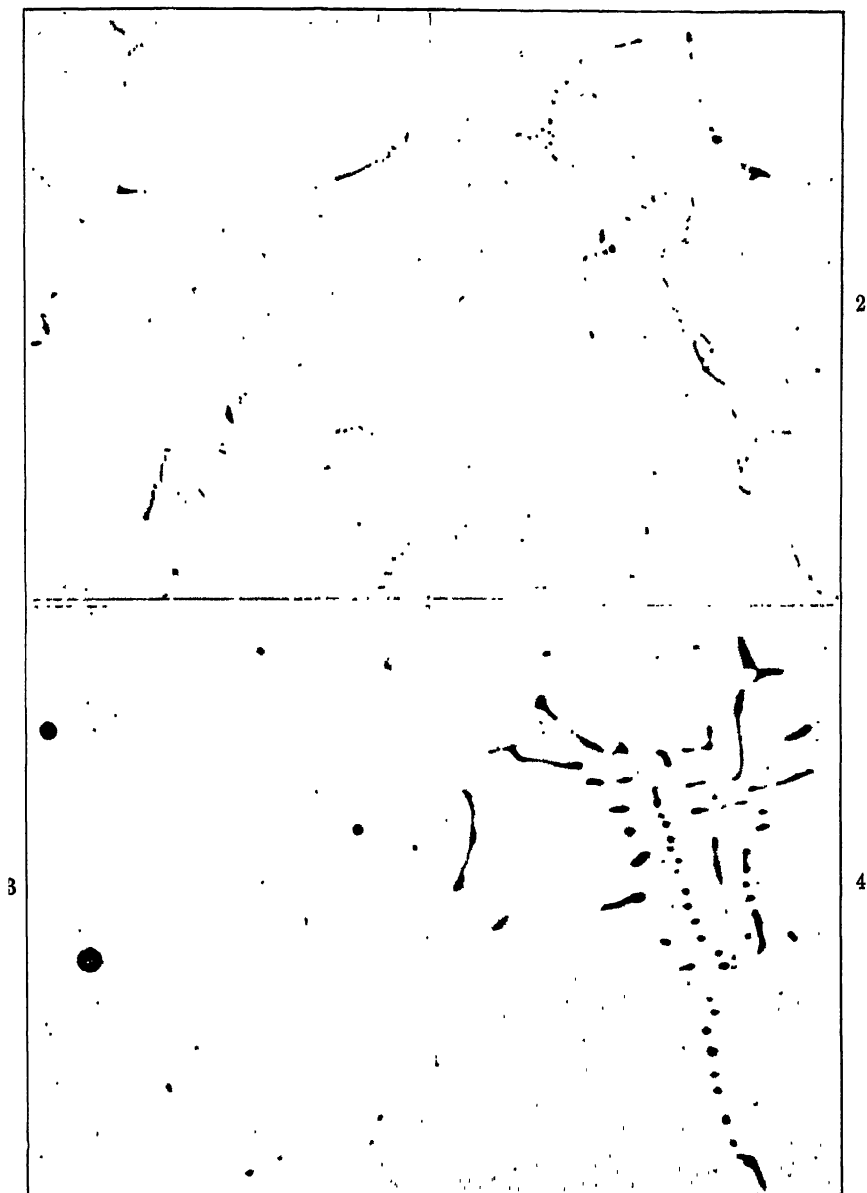


FIG. 1.—ACID ARC-FURNACE HEAT 255. $\times 250$.
Example of steel with low ductility due to Al addition.

FIG. 2.—ACID ARC-FURNACE HEAT 256. $\times 250$.
Example of steel with low ductility due to Al addition.

FIG. 3.—ACID ARC-FURNACE HEAT 257. $\times 250$.
Example of steel with high ductility in spite of Al addition.

FIG. 4.—INDUCTION-FURNACE HEAT 30. $\times 500$.
Eutectic type of inclusions in steel not treated with Al.

A study of the problem was undertaken at the research laboratory, and soon it was observed that there was a characteristic and consistent relation between the ductility and the type of inclusions present. It was noticed, for instance, that when aluminum was added to a deoxidized steel, not only were fine dustlike groups of alumina produced but a profound change usually took place in most of the other nonmetallic inclusions. Accompanying this change in the inclusions is a decrease in ductility, principally in the reduction of area, although the elongation is also affected. Occasionally the addition of aluminum does not produce this characteristic change in the inclusions, and when it does not, the ductility is likewise unaffected. Sometimes low ductility is found in steels that have not been treated with aluminum, but in these steels is found a type of inclusion similar to those produced by the addition of aluminum.

In Figs. 1 to 3 are shown the unetched micrographs of three typical heats from a 3-ton acid electric-arc furnace. The compositions and physical properties of these steels are given in Table 1. Although the

TABLE 1.—*Typical Heats from 3-ton Acid Electric-arc Furnace*

Heat No.	Composition, Per Cent					Physical Properties			
	C	Mn	Si	P	S	Yield Point, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation in 2 In.	Reduction of Area, Per Cent
255 ^a	0.23	0.69	0.40	0.021	0.042	42,250	73,900	21.5	27.2
256 ^a	0.24	0.77	0.54	0.020	0.044	50,000	80,500	19.0	22.3
257 ^a	0.23	0.63	0.41	0.021	0.040	42,750	71,650	30.0	53.3
30	0.469	1.21	0.69	0.022	0.045	70,500	116,200	18.0	28.0
32	0.468	1.31	0.75	0.021	0.040	72,650	122,500	21.0	44.0

^a Treated with aluminum in ladle at furnace spout.

compositions are similar, there is a marked difference in the ductility. Figs. 1 and 2 have the type of inclusion characteristic of nonductile steel. Fig. 2 is somewhat more pronounced than Fig. 1 and also has lower ductility. Fig. 3 is equally characteristic of a ductile steel. Aluminum to the amount of about 12 oz. per ton was added in the ladle to all three of these heats. While the aluminum addition produced its usual effect on the inclusions and ductility of Figs. 1 and 2, it did not have a similar effect on Fig. 3. This last example illustrates the statement made above that the addition of aluminum to steel does not affect the ductility unless it also changes the nature of the inclusions. The inclusions in Fig. 3 are the kind that would ordinarily be expected were no aluminum added.

There are shown in Figs. 4 and 5 two steels of similar composition but of higher carbon and manganese than those of Figs. 1 to 3. The



FIG. 5.—INDUCTION-FURNACE HEAT 32. $\times 500$.
High ductility.

FIG. 6.—INDUCTION-FURNACE HEAT 199. $\times 250$.
Intermediate ductility.

FIG. 7.—INDUCTION-FURNACE HEAT 208. $\times 250$.
Treated with calcium silicide. Intermediate ductility.

FIG. 8.—INDUCTION-FURNACE HEAT 207. $\times 250$.
Treated with calcium silicide. Angular inclusions. Intermediate ductility.

latter steels were made in a high-frequency induction furnace under similar conditions and were given the same heat treatment. The analysis and physical properties are given in Table 1. No aluminum was added to either steel; yet it is readily seen that No. 30 has the type of inclusions that unmistakably marks it for a steel of low ductility, while No. 32 is just as plainly stamped for high ductility. Table 1 proves No. 32 to be superior in strength as well as in ductility. The higher manganese content probably accounts in part for the higher strength of No. 32.

Although the examples just referred to are considered typical rather than extreme, many intermediate structures are found which have intermediate ductilities corresponding to the inclusions. Photomicrographs of two such steels are shown in Figs. 6 and 7. These steels have both the globular inclusions of ductile steel and the elongated chain type of low-ductility steel. Of these steels, one (No. 199) had no special deoxidizer added, while the other (No. 208) was treated with calcium silicide. Another type of inclusion which confers intermediate ductility is shown in No. 207, Fig. 8. This is referred to as the angular or free-formed crystalline type of inclusion. It seems to occur most frequently in steels containing over 1 per cent of manganese. Calcium silicide was used in deoxidizing this steel.

But for lack of space, numerous other examples could be cited. Hundreds of specimens of steel have been examined microscopically, and a most remarkable consistency has been found between the ductility and the nature of the inclusions. Due allowance must be made, of course, for the composition of the steel. This relation has been found so consistent, in fact, that the ductility of a cast steel can be predicted after a microscopic examination. In test cases, steels have been placed in the order of their ductilities before the physical tests were made and in no case has there been an error made except where the difference in ductility has been so slight as to be negligible.

The factor on which it is desired to place greatest emphasis is that it is not the amount of inclusions that directly affects the ductility but rather the arrangement of the inclusions that are there. The reason for the strong emphasis on this point is that this rather obvious conclusion has been reached so seldom and by so few observers. A notable exception is G. F. Comstock,¹ who has charged aluminum additions with causing the sulfides to be arranged in streaks in a sort of fragmentary network, and this network of sulfides in turn with being largely responsible for the low ductility.

References too numerous to mention can be found in the literature, attributing the low ductility of aluminum-treated steel to a few inclu-

¹ G. F. Comstock: Aluminum and Titanium as Deoxidizers. *Iron Age* (Dec. 4, 1924) 1477.

sions of alumina. These alumina inclusions usually occur in such small and widely scattered groups as shown in Fig. 19. Ordinarily they are so scarce that they will not show in a photomicrograph unless they are intentionally included. No logical explanation has ever been advanced, to the writers' knowledge, as to why these relatively few groups of alumina should have any more effect on ductility than the inclusions found in steel not treated with aluminum. They occur in most steels to which aluminum has been added, but the authors believe that they have an insignificant influence on ductility. It has already been shown (Fig. 4 and Table 1) that low ductilities are possible in the absence of alumina when the inclusions are of a certain type.

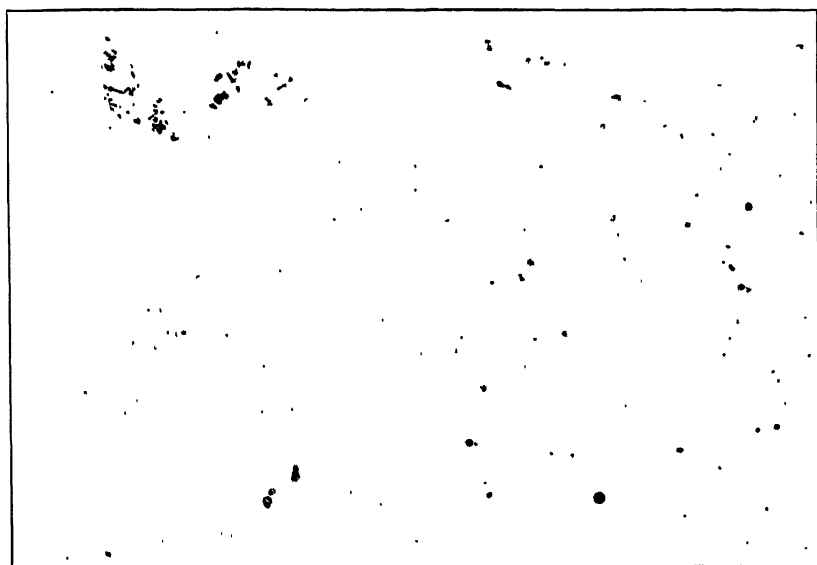


FIG. 9.—INDUCTION-FURNACE HEAT 564. $\times 200$.

Alumina or aluminum silicate inclusions at top of cut.

FIG. 10.—INDUCTION-FURNACE HEAT 534. $\times 100$.

Example of "dirty" steel with high ductility.

On the other hand, a steel may hold considerable alumina and still have good ductility; for instance, heat 564, Fig. 9, shows a steel that contains scattered groups of alumina inclusions (Composition: C, 0.266 per cent; Mn, 0.68; Si, 0.41; P, 0.014; S, 0.031) and yet has the following properties in the normalized state:

Ultimate strength, lb. per sq. in.....	76,800
Yield point, lb. per sq. in.....	47,550
Elongation in 2 in., per cent.....	32.5
Reduction of area, per cent.....	56.0
Izod impact, ft-lb.....	39.0

In spite of the presence of alumina, the other inclusions are globular and random in their arrangement, which accounts for the high ductility. Such a steel is not apt to occur in usual steelmaking practice, and this one was produced especially to test this point. The procedure was first to deoxidize an induction-furnace heat in the usual manner with ferromanganese and ferrosilicon. Then, an amount of aluminum wire equivalent to 2.2 lb. per ton of steel was added and allowed to diffuse. This unusually large quantity of aluminum accounts for the large groups of alumina inclusions. Third, a quantity of iron ore was added, and after a short time allowed for reaction, the heat was poured into a standard 60-lb. test block.

Unfortunately, no steels have yet been produced free from nonmetallic inclusions and therefore no data on the physical properties of such hypothetical steels are available. However, the quantity alone of inclusions in the range of amounts ordinarily found in cast steels does not seem to have any marked effect on the strength, ductility and impact values of the steel; and considerable doubt is felt as to whether any considerable improvement would be found in the properties of so-called "clean" steels. It is certain, on the other hand, that a steel can be "dirty" and still have excellent physical properties providing the inclusions are of the right type. A good example of this is the steel of heat 534, the photomicrograph of which is shown in Fig. 10. This is regarded as a rather dirty steel; yet in the normalized condition, it had the following properties:

Tensile strength, lb. per sq. in.....	108,800
Yield point, lb. per sq. in.....	85,900
Elongation in 2 in., per cent.....	28.0
Reduction of area, per cent.....	60.8
Izod impact, ft-lb.....	60

There being so few reliable data concerning the effect of inclusions on the endurance value of steel, this phase of the physical properties is omitted from the discussion.

REASONS FOR DIFFERENCE IN DUCTILITY

A close study of the photomicrographs in Figs. 1 to 5 clearly reveals the reason for the variation in ductility with different types of inclusions. Those accompanying high ductility as represented by Fig. 3 (No. 257) and Fig. 5 (No. 32) have the following essential characteristics. They vary greatly in size but are practically all globular in shape and are distinctly random in their arrangement and distribution. There are usually three kinds: the dark colored silicates, the light gray sulfides, and those containing substantial portions of both sulfide and silicate. Probably all have some of both sulfide and silicate, as they are practically miscible

in the liquid state.² But the really important point is that they are true inclusions occurring mostly within the crystals of steel and leaving the latter in a continuous coherent phase. Thus there is the very minimum of interference with the plastic distortion of the steel.

When there is low ductility, as represented by Figs. 1 and 2 (Nos. 255 and 256) and Fig. 4 (No. 30) the inclusions have an utterly different character. When this type is the result of aluminum additions, small scattered groups of dustlike particles of alumina are present, but these are usually so scattered and few as to be rather inconspicuous. The other inclusions occur as elongated club-shaped particles or chains of round, evenly sized and spaced dots. It is probable that those appearing round are really elongated inclusions shown in cross-section. They are confined exclusively to the grain boundaries of the primary crystals or dendritic fillings, and have all the earmarks of being a part of a eutectic that was the last mother liquor to solidify. More evidence that they are in fact a part of a eutectic formation will be given later. Occurring as they do, they form a continuous network or envelope about all the primary crystals of steel. Thus they constitute the continuous or external phase, with the steel crystals forming the discontinuous or internal phase. Or to be more exact, since a phase must be homogeneous, this eutectic is a matrix in which the crystals of steel are embedded. These primary crystals or dendrites must not be confused with the grains or crystals as seen under the microscope after the steel has cooled down to room temperature and is in the alpha state. This eutectic appears to be brittle, and when plastic deformation occurs, it cracks before the metal within has much chance to flow. This results in an amorphous, woody type of fracture and consequent low ductility. While there often appears to be a lower total quantity of inclusions in aluminum-treated steel, they are strategically arranged to work the greatest harm to the ductility.

EVIDENCE OF SOLUBILITY OF INCLUSIONS

The foregoing argument is obviously based on the premise of the solubility of inclusions in liquid steel. This premise is strongly supported by the evidence accumulated during the present investigation. The possibility of the solubility of inclusions in liquid steel has been discussed from time to time but has not been accepted generally by metallurgists. Ziegler³ suggested the solubility of inclusions in gamma iron as well as in liquid steel. Probably the most comprehensive discussion of this subject is by Wohrman,⁴ who points out that although the solubility of

² D. M. Levy: Iron and Steel Inst., *Carnegie Schol. Mem.* (1911) 3, 260.

³ M. Ziegler: Sur le Crystallization du Fer Alpha. *Rev. de Mét.* (1911) 655 et seq.

⁴ C. R. Wohrman: Inclusions in Iron. *Amer. Soc. Steel Treat.* (1928) 14, 542-548.

iron oxide and iron sulfide in liquid iron has been proved, the solubility of the mixed sulfides and silicates has been neither proved nor disproved. He does give evidence that strongly indicates that a considerable number of these inclusions are actually dissolved in liquid iron.

Observations made almost daily during the three years during which the present data were collected have led inevitably to the conclusion that the common inclusions of steel, with the probable exception of alumina, are to a large degree soluble in the molten steel. They form as inclusions during the cooling and solidification of the steel.

One of the earliest and most persistent phenomena observed was the fact that small castings invariably contained small inclusions, while large castings just as surely carried proportionately larger inclusions. This was extremely puzzling until explained by the hypothesis of solubility. An interesting example of this occurred during some tests at one of the plants. These tests were run on a basic open-hearth furnace and were for the purpose of trying out some recently advanced theories. Certain samples were taken which, when examined under the microscope, showed no inclusions at all. Had clean steel really been produced? The samples were sent to the research laboratory for checking, and when higher magnification was used the steel was found to contain quantities of very small inclusions which had been almost indiscernable at the lower magnification. It turned out that the samples had been cast as small pieces in chill molds, which accounted for the small size of the inclusions. Steel cast against a chill always has very small inclusions close to the chill, and they increase in size with distance from the chill.

There is no change in either the size or quantity of inclusions with time of holding in the liquid state, providing other things are equal. Probably everyone who has contemplated the problem of elimination of inclusions has conceived the idea of holding the steel in the liquid state for a sufficient time to allow the inclusions to rise to the surface and enter the slag. This method has been tried by nearly everyone who has had the opportunity, including the authors, and with universally disappointing results. The method will not work and it must be because the inclusion-forming material is not in a condition to rise. Calculations⁵ have been made as to the rate at which inclusions of various sizes would rise, and some of the larger ones are given rates of several feet per minute. Proof that undissolved foreign material actually does rise rapidly in steel is given by the fact that accidental inclusions of sand, bottom material, etc. are so rarely seen in steel.

In order to obtain experimental evidence on the foregoing observations, the following experiment was made. The experiment was repeated for purpose of checking, but the results were in such close agreement that

⁵ U. S. Bur. Mines *Rept. of Investigations* 3081 (1931).

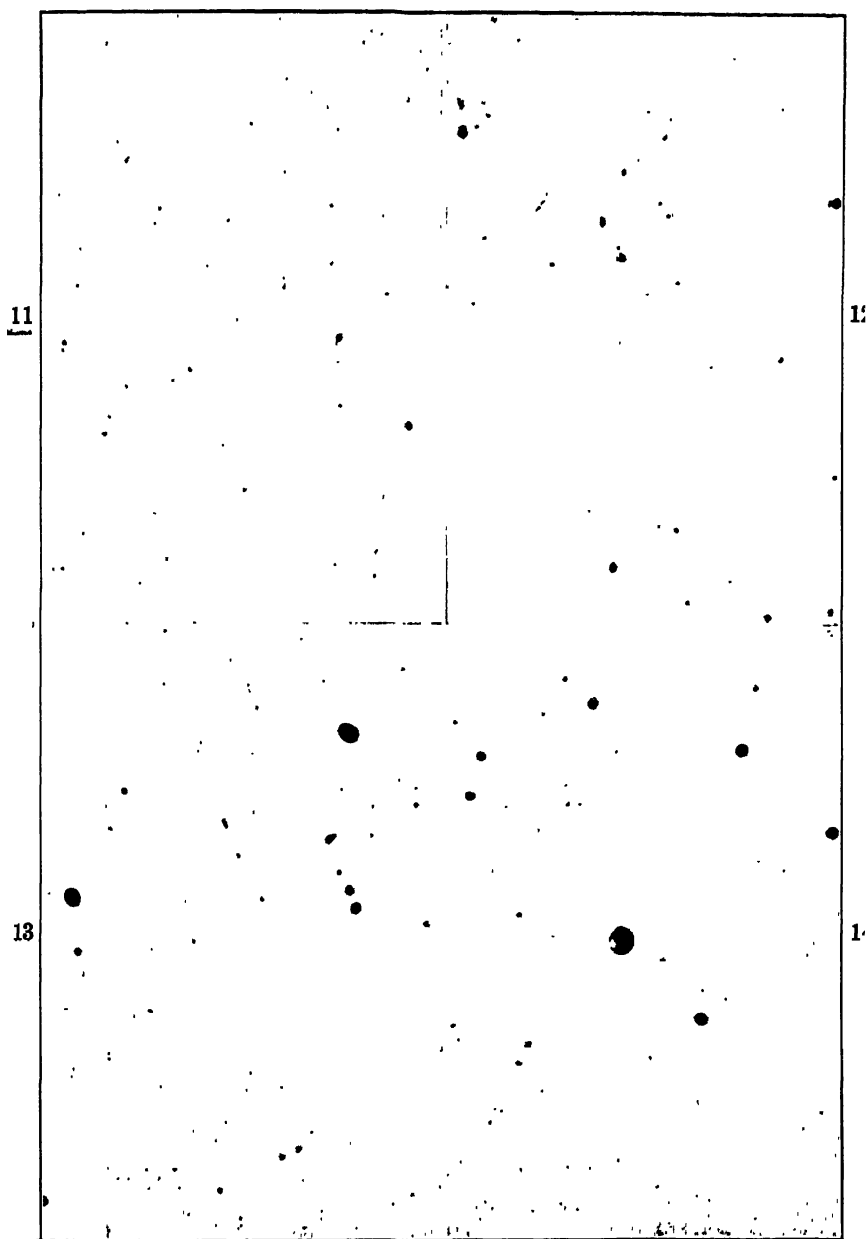


FIG. 11.—OPEN-HEARTH STEEL CAST IN SAND AS $\frac{1}{4}$ -IN. SECTION. $\times 100$.
FIG. 12.—OPEN-HEARTH STEEL CAST IN SAND AS 1-IN. SECTION. $\times 100$.
FIG. 13.—OPEN-HEARTH STEEL CAST IN SAND AS 3-IN. SECTION. $\times 100$.
FIG. 14.—OPEN-HEARTH STEEL CAST IN SAND AS 6-IN. SECTION. $\times 100$.

results of only one experiment are reported. A heat (composition: C, 0.266 per cent; Mn, 0.77; Si, 0.36; P, 0.029; S, 0.041) was made in an acid open-hearth furnace, using standard practice. A bifurcated spout was used in tapping, and 6 tons was run into a small ladle while the other 20 tons was run into a larger ladle. To the small ladle was added 6 lb. of aluminum or 1 lb. to each ton of steel. It was tapped at 3:05 p. m. Twenty minutes later, between 3:25 and 3:31, a series of test blocks was cast from the small ladle. In this series, there were blocks of $\frac{1}{4}$ -in., 1-in., 3-in., 6-in., 9-in., 12-in., and 15-in., section, all gated at the bottom and cast in dry sand. At 3:27, or 22 min. after tapping, a 9-in. block was cast from the large ladle, and then from 3:48 to 3:52, or 45 min. after tapping, a series like the above, running from $\frac{1}{4}$ to 15 in. was cast. Risers as large as the blocks themselves were used on all these castings, to insure solidity and to allow entrapped dirt, etc. to float out of the portion to be used.

Specimens for microexamination were cut from the center of each of these sections. Photomicrographs in the unetched condition of the specimens taken from the blocks cast from the large ladle are shown in Figs. 11 to 18. No aluminum was used in these, and it will be noted how uniformly rounded all the inclusions are. The particular spot selected for each picture was chosen because it had the largest inclusions to be found in that specimen. While there is a great variety of sizes of inclusions in each section, it is readily seen that there is a consistent increase in the average and maximum size of the inclusions with increase in the section of the casting; in other words, the average size of the inclusion in a given heat of steel is dependent on the rate of solidification. This signifies, in turn, that the inclusions are formed during solidification and therefore do not exist as such prior to it.

Although this steel was held in the ladle for 45 min., there is no dearth of inclusions. Likewise, in the two 9-in. sections, one of which was cast 22 min. after the tap and the other 23 min. later, there is no noticeable difference in either the size or quantity of inclusions. Holding time is apparently without influence on the quantity of nonmetallics held, which, of course, is quite in line with the theory of solubility.

An integration of the inclusions by the inclusion-count method will show an apparently greater amount of nonmetallics in the large sections, like the 12-in. or 15-in. sections, than can be seen in the small sections, such as the $\frac{1}{4}$ -in. or 1-in. sections. All sections having been poured consecutively from the same ladle of steel, it is obviously impossible to have an actual difference in nonmetallic content. Indeed, if there could be a difference, it would seem, on the basis of current beliefs, that the sections with the larger inclusions would be cleaner. There may be some segregation of inclusion-forming material toward the center of a heavy section, but in the $\frac{1}{4}$ -in. section, for example, there are many small inclusions ranging down to the smallest that can be detected with the

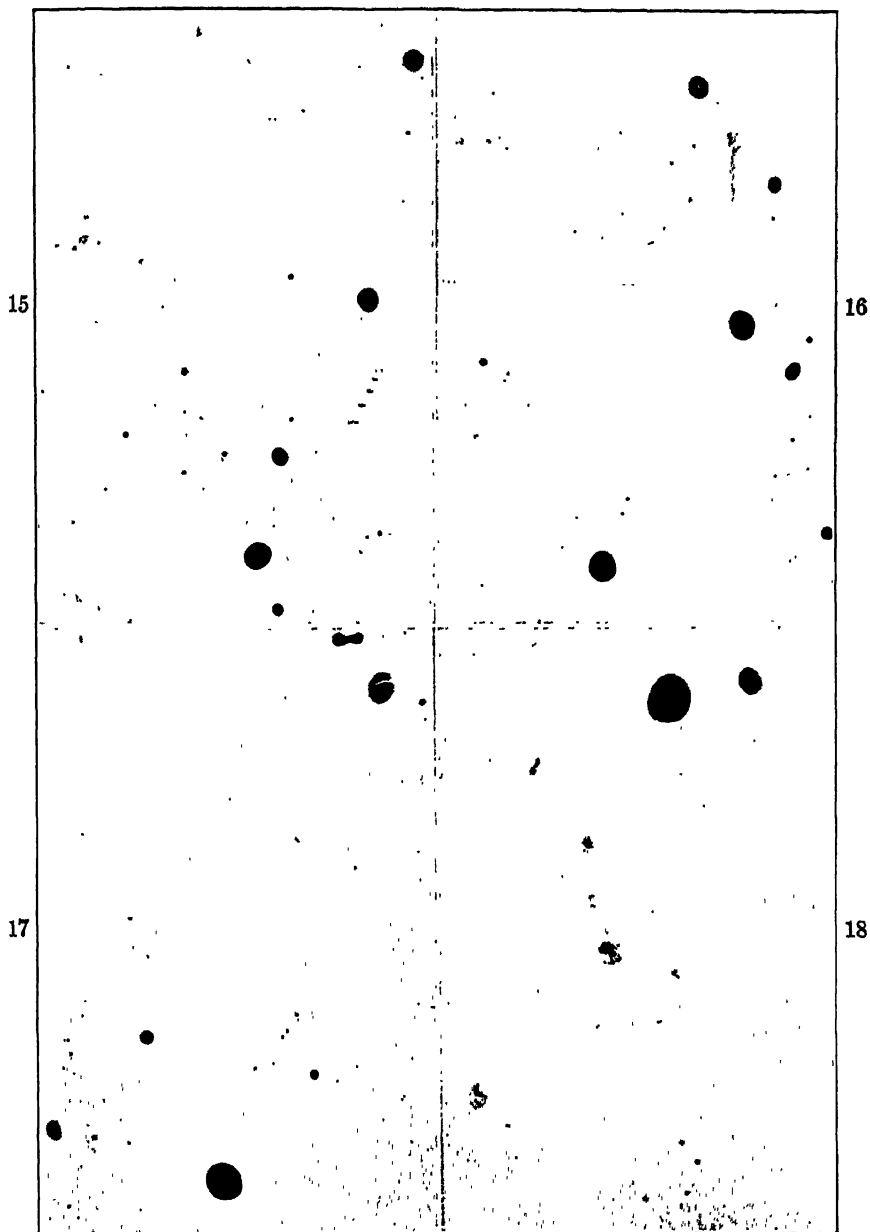


FIG. 15.—OPEN-HEARTH STEEL CAST AS 9-IN. SECTION 22 MIN. AFTER TAP. $\times 100$.
FIG. 16.—OPEN-HEARTH STEEL CAST AS 9-IN. SECTION 45 MIN. AFTER TAP. $\times 100$.
FIG. 17.—OPEN-HEARTH STEEL CAST AS 12-IN. SECTION. $\times 100$.
FIG. 18.—OPEN-HEARTH STEEL CAST AS 15-IN. SECTION. $\times 100$.

microscope. It is logical to suppose that they do not end there and that there are others of submicroscopic size, perhaps some bordering on a condition of molecular dispersion. With steel solidifying so quickly, there is little time for the preferential precipitation of the nonmetallics in solution or for the agglomeration of the inclusions after their formation.

In all sections there is a wide range of sizes in the inclusions, even the $\frac{1}{4}$ -in. section having a few fair-sized ones. This seems to indicate that the solubility of the nonmetallics is limited and varies with the temperature. As the steel cools toward the freezing point, a few inclusions are formed first. Then as the temperature drops and the solubility further decreases, the nonmetallics are preferentially precipitated on those already formed, although new ones are forming constantly. At about the freezing point, when the solubility changes rapidly, there is a more sudden precipitation of very small inclusions. The statement that high temperature increases the solubility for nonmetallics has been verified by numerous observations. Very hot heats are "dirty." Heat 534, shown in Fig. 10, was hotter than the average heat.

Although in this discussion numerous references are made to the amount of nonmetallics present as inclusions, let it be understood that no actual quantitative determinations were made. Unfortunately, there was no opportunity for work on this subject. Opinions given are based on a careful scanning of a polished section under the microscope in comparison with other steels. This is roughly equivalent to an inclusion count and, although one might easily be mistaken in estimating two steels very similar, any large difference would be readily detected. Allowance is always made for the size of the section as cast. It is pertinent to mention here that no large differences have been found in the quantity of inclusions in steels made by ordinary processes. One of the outstanding observations has been that in steels of not too great a difference in composition, whether made in the open-hearth furnace, arc electric furnace, or high-frequency induction furnace, with day-to-day variations in practice, year in and year out, there are but slight variations in the quantity of inclusions. Heat 534, Fig. 10, has been mentioned as an unusually dirty steel, but from the pictures shown, it will take careful comparison to see that it is any worse than the 1-in. section of Fig. 12. There are factors that operate to vary the character and quantity of inclusions, the most important being composition and temperature. These will be discussed later. A high sulfur content is certain to be accompanied by a high inclusion content.

Is not this regularity of inclusion content a further evidence of solubility, and does it not attest that the inclusions are present to the saturation point? Any amount over the saturation point seems to be quickly eliminated from the bath. Of course, it can be argued that the iron oxide present in the steel before deoxidation controls the quantity of

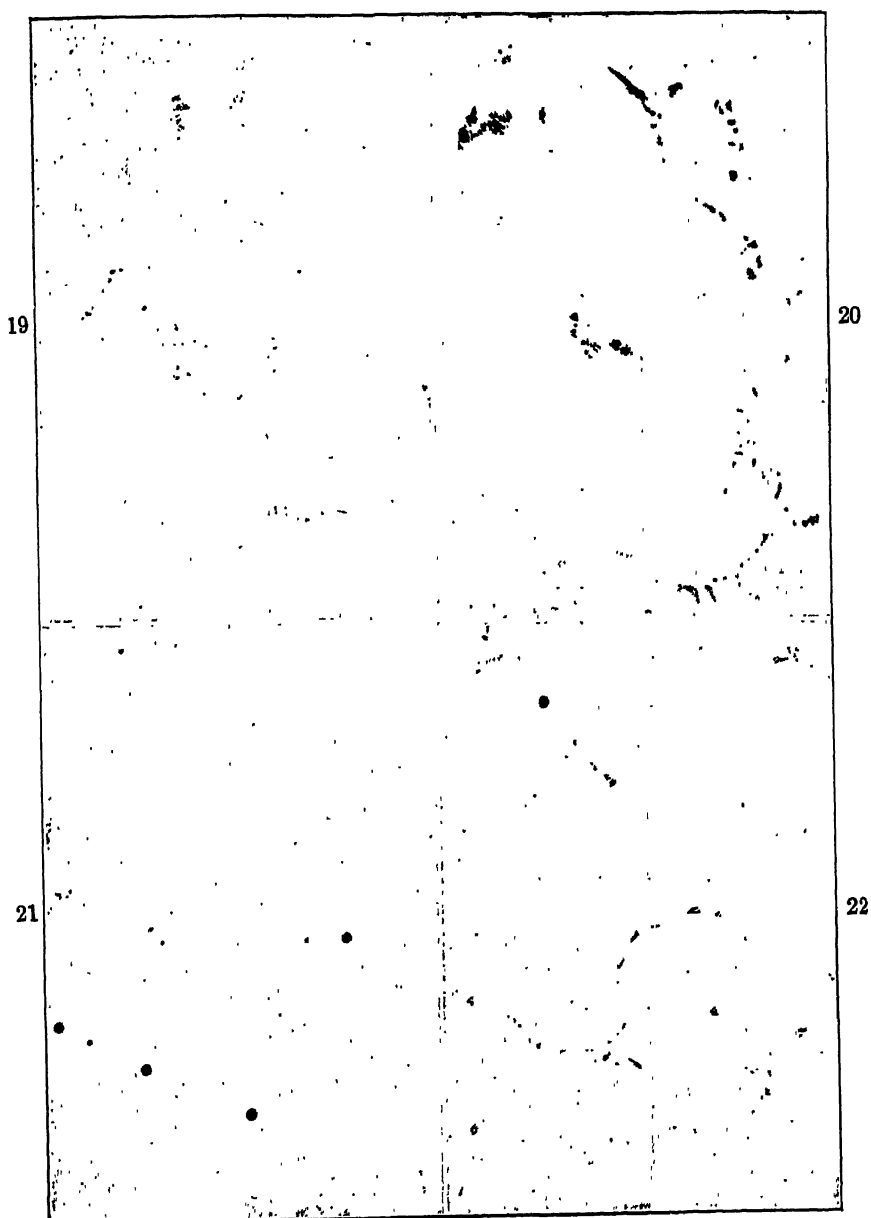


FIG. 19.—OPEN-HEARTH STEEL CAST AS 1-IN. SECTION. $\times 100$.

Treated with Al in ladle. Alumina or aluminum silicate group at top.

FIG. 20.—OPEN-HEARTH STEEL CAST AS 9-IN. SECTION. $\times 100$.

Treated with Al in ladle.

FIG. 21.—OPEN-HEARTH STEEL CAST IN DRY SAND MOLD WITH NO Al ADDITION. $\times 200$.

FIG. 22.—SAME AS FIG. 21, BUT WITH Al ADDED IN POURING CUP OF MOLD. $\times 200$.

inclusions formed, and that iron oxide having a limited solubility, the inclusions must also be limited. This is undoubtedly true to a great extent, as will be shown later, but if inclusions were being eliminated from the time of deoxidation to solidification there would certainly be larger variations than have been found. Furthermore, there is great uniformity and consistency in the inclusions throughout all the steel of a given heat, provided the cooling conditions are similar. A certain degree of concentration of inclusions is known to exist where the zone of columnar dendrites ends in an ingot, and also in the risers or sink heads of castings and around shrinkage cavities; and, of course, the inclusions are larger in the center of a heavy section than near the surface.

In the series cast from aluminum-treated steel there was a similar effect due to size of section up to 6 in.; above 6 in., there was little change. Figs. 19 and 20 show the 1-in. and 9-in. sections. The same characteristics are found in both sections, the only difference being that everything is on a larger scale in the 9-in. section. With the exception of the clusters of alumina (or aluminum silicate), the inclusions are confined to the dendritic fillings. In the larger section, the rate of cooling was slower and the primary crystals larger. This caused a greater concentration of the inclusions into broader and coarser bands than in the smaller section, but they have not varied in the least from the habits of a eutectic; in fact, the larger section shows the eutectic formation to greater advantage. Even the aluminum silicate particles are larger and are in bigger clusters in the large section, which seems to indicate at least slight solubility for them.

As has been mentioned earlier, when aluminum is added to steel already deoxidized with manganese and silicon, a profound change usually takes place in the character of the inclusions to the detriment of the ductility. This change takes place with great rapidity, as will be shown by the results of the following experiments. Two standard test-bar molds made of dry sand, thoroughly dried and still warm from the drying oven, were placed side by side. These were poured consecutively from the same ladle of plain carbon steel, with the difference that in the second a piece of $\frac{1}{8}$ -in. aluminum wire was fed into the stream of metal as it entered the downgate. This was repeated with two dry sand molds which were only partly dried, two green-sand molds which were skin dried by being allowed to stand open for about two hours, and two green-sand molds that were moistened on the surface with a fine spray of water just before they were closed.

The test bars were normalized by heating to 1600° F. for 2 hr. and cooling in air. The physical results are given in Table 2. Attention is called to the striking similarity in the properties of all the bars poured without addition of aluminum and to the uniformity with which the aluminum affected the properties of the others. The aluminum had

TABLE 2.—*Results on Test Bars with and without Aluminum*

Composition of steel: C, 0.278 per cent; Mn, 0.79; Si, 0.37; P, 0.030; S, 0.035.
Heat treatment: 1600° F. for 2 hr. Cooled in still air.

	Yield Point, Lb. per Sq. In.	Ultimate Strength Lb. per Sq. In.	Elonga- tion, Per Cent in 2 In.	Reduction of Area, Per Cent	Average Isod Impact, Ft-lb.
Well dried dry sand mold. No Al used.	47,300	78,900	31.5	54.4	37.0
	47,800	79,100	31.0	54.9	
Well dried dry sand mold, 0.05 per cent Al added.	50,600	79,550	26.5	38.2	31.0
	47,900	79,200	27.0	42.0	
Half dried dry sand mold. No Al used.	46,200	79,500	31.5	57.0	37.0
	47,200	79,500	30.5	54.4	
Half dried dry sand mold, 0.05 per cent Al added.	51,000	80,150	26.5	37.6	29.0
	51,250	79,600	26.5	38.9	
Air-dried green-sand mold. No Al used.	47,300	79,300	32.0	51.5	38.5
	45,100	79,400	31.5	56.6	
Air-dried green-sand mold, 0.05 per cent Al added.	49,650	78,950	26.0	36.0	27.0
	48,900	79,400	25.0	36.6	
Moistened green-sand mold. No Al used.	44,350	78,800	31.5	55.7	37.0
	47,700	79,200	31.5	56.0	
Moistened green-sand mold, 0.05 per cent Al added.	49,550	79,250	24.5	34.6	26.5
	50,450	80,000	25.0	35.7	

the effect of increasing the yield point and decreasing the ductility and impact resistance. This is cited because it has been claimed⁶ that aluminum affects steel chiefly when alumina is formed by oxidation of the aluminum by migrant gases in the mold. These migrant gases are supposed to occur only in improperly prepared molds. This experiment shows, however, that the condition of the mold has little to do with the effect of aluminum on the ductility of the steel.

The character of the inclusions in the various types of mold was so similar that only photomicrographs of the first two are shown in Figs. 21 and 22. Again, the interrelation of ductility and type of inclusion is clearly illustrated. In this case, both the inclusions and the ductility are not affected as much as in heats 255 and 256 of Figs. 1 and 2. The time interval between the addition of the aluminum and the solidification of the steel was probably not over one minute, it being cast as a 1-in. section; yet there was time for this change to take place. Had the inclusions shown in Fig. 21 existed as such before the aluminum addition, there must certainly have been insufficient time for the highly diluted aluminum to have wrought such a change. The reaction would be

⁶ G. Batty: The Interrelationship of the Pin Hole Trouble and the Low Ductility Problem. *Trans. Amer. Foundry Assn.* (May, 1931).

limited to the surface of the inclusions and could progress only as fast as the aluminum could diffuse to the inclusions. Large inclusions would have to be broken into smaller ones and the very small ones agglomerated into larger ones, for after the aluminum addition, there is considerable uniformity in size. But if one considers the nonmetallics as being in solution, all the difficulties of explanation disappear. Speed of reaction is limited only by the rate of mixing and diffusion of the aluminum, and the inclusions are free to form in their natural manner without regard to the way in which they would have formed had the aluminum not been added.

A similar test was carried one step further in heat 564, as shown in Fig. 9. In this, iron ore was added 1 min. after the aluminum addition, and the steel was poured 1 min. later. Instead of the characteristic structure produced by aluminum, the inclusions are all globular and scattered except for the clusters of alumina. The alumina inclusions (which are probably aluminum silicate) are practically unchanged, and this is regarded as evidence that they, unlike the iron-manganese silicates and iron-manganese sulfides, are largely insoluble.

WHAT CAN BE DONE ABOUT INCLUSIONS

One of the puzzling things about steelmaking has been that occasional "bad" heats have been produced for which no definite reason could be assigned. They might be made in approximately the same manner and from the same material as "good" heats, and have almost the identical composition, but the bad heats seem to have an inherently inferior ductility and general stamina. These off heats seem to be sluggish and do not fill out the molds well. The so-called "overreduced" steel⁷ is an example of these off heats. In the authors' own experience, steels very close in composition and made by what seemed, at the time, to be identical practice, have been compared and have been found to vary as much as 50 per cent in elongation and 100 per cent in reduction of area. It has been observed that electric-furnace steel is more prone to these off heats than open-hearth steel and that the prevalence increases rapidly with increase in carbon content. Many of these off-color heats with low ductility have been examined and compared with better steel. Invariably the microscope revealed the condition that has already been described at length; namely, the low-ductility steels had the eutectic type of inclusions, while those of high ductility had the scattered globular type. The accusation being thus placed directly on the inclusions, the question arose as to what remedy could be applied.

If the inclusions could be eliminated, presumably most of the troubles would disappear, but at present there is no known method of accomplish-

⁷ J. V. McCrae, R. L. Dowdell and L. Jordan: A Study of the So-called "Overreduced" Condition in Molten Steel. U. S. Bur. Stds. *Jnl. of Research* (November, 1930).

ing this end, and it never happens accidentally. If steel could be made sulfur-free, a large portion of the inclusions would be automatically eliminated. The fight against sulfur has already been waged for years. Vacuum melting and casting offers considerable promise for cleaner steel but as yet is undeveloped. It is to be sincerely hoped that some day a method for producing "clean" steel will be perfected. The apparent solubility of the inclusion-forming material indicates that it is a more difficult problem than has been anticipated. In the meantime, there are the inclusions to contend with. The thought occurred to the authors that inasmuch as the inclusions occur sometimes in a benign condition, they could always be made to take this harmless form if the proper conditions were known. Accordingly, experiments were conducted to see what could be done in that direction.

In the early heats in the arc furnace with an acid hearth, it was found necessary to make a general use of aluminum in order to prevent excessive porosity in the castings. The aluminum did not always give freedom from porosity but it did usually greatly decrease the ductility. However, there were occasional heats that despite the aluminum had very satisfactory ductility. Moreover, these ductile heats handled well, were quite fluid, and as a rule gave sound flawless castings. One of the first indications of the cause for these unusual heats was obtained when an experimental heat was made in which four times the usual quantity of iron ore was used. Contrary to some predictions, this heat was excellent in every respect, showing good ductility even though aluminum was added to the ladle in the proportion of about 1 lb. per ton of steel.

In this case severe oxidation of the bath had turned the trick and had given desirable results. This was checked up and was found to be consistent. Earlier, a special test heat had been made by quite the opposite procedure. Thinking to take advantage of the electric furnace's reputed ability to maintain a neutral or reducing atmosphere, it was decided to run with the very minimum of oxidation. A charge of clean scrap was selected with a carbon content so low that no oxidation was necessary to attain the desired composition. It was melted down under a light brown translucent slag, which was practically free of ferric oxide. Here was a steel that should be all that could be wished for! It could not be gassy because it was being deoxidized continually from the beginning of the melt down! Additions of ferrosilicon and ferromanganese were made in the furnace and a little aluminum was added to the ladle. The latter was not considered necessary but was added merely as a precaution. This steel literally effervesced in the molds and was so gassy that not even a test bar could be obtained. It was also sluggish and tended to plug the nozzle.

Another experiment concerned a heat of steel that had been treated with 1 lb. of aluminum per ton, put in the ladle at the time of tapping.

A standard test block was poured, and then immediately afterwards, 100 lb. was tapped into a hand ladle. While it was pouring into the hand ladle, 150 grams of iron ore was added and mixed by the agitation of the stream of metal. It was then poured into a similar test block mold. A comparison of the physical results is shown in Table 3. Micro-

TABLE 3.—*Results on Aluminum-treated Steel with and without Iron Ore Added*

	Yield Point, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elonga- tion in 2 In., Per Cent	Reduction of Area, Per Cent	Fracture
Direct from ladle.....	51,400	79,850	23	25.8	Woody
Treated with iron ore.....	47,600	78,800	37	51.1	½ cup

scopic examination showed clearly the reasons for this difference. The steel direct from the ladle had the eutectic type of inclusion, while in the steel treated with iron ore the inclusions had somehow been transformed to the globular scattered type.

Experiments were continued in the high-frequency induction furnace. Although conditions in this furnace are somewhat different from either the open-hearth or arc electric furnace, the basic principles of steelmaking are the same in any furnace. It is not the practice to use aluminum in the steel from the induction furnace except in special heats where its effect is being studied. Even so, the ductilities varied a great deal, and it became very urgent to find out why. This was especially true with the higher carbon alloy heats where the carbon ran 0.35 per cent or more. The fact that the trouble seemed to be in proportion to the carbon content suggested that the carbon might have an influence. Nearly all of the tests were run on higher carbon contents, the idea being that if they could be made satisfactorily the low-carbon steels would be automatically taken care of.

Certain conditions were found to be of advantage in giving high ductility to steels which ordinarily gave a large proportion of low-ductility heats. If the carbon content of the bath was kept low until very near the end of the heat, high ductility usually resulted. Recarburization after the alloy additions was best, but the steel was apt to be gassy. Recarburization just previous to the alloy additions worked well and gave sound steel. Adding a small amount of iron ore and allowing it just time enough to dissolve before adding the deoxidizer gave very good results.

Adding the ferromanganese ahead of the ferrosilicon showed advantage over adding them together or with the ferrosilicon first. Using mixed alloys, like silicomanganese of any ratio, was better than ferromanganese and ferrosilicon. One annoying mystery apparently was

cleared up when it was found that a variation in the temperature of the metal at the time of deoxidation often made a notable difference in the inclusions and resultant ductility. If the metal was very hot just before the deoxidizers were added, it was ductile; if rather cool, the ductility was low even though the temperature was increased afterwards. An example of this is shown in heats 498 and 499, the composition and properties of which were as shown in Table 4.

TABLE 4.—*Composition and Properties of Heats 498 and 499*

Heat No.	Composition, Per Cent					Yield Point, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction of Area, Per Cent	Isod Impact, Ft.-lb.
	C	Mn	Si	P	S					
498	0.636	1.41	0.40	0.015	0.034	72,500	135,950	14.0	22.3	4.5
499	0.624	1.33	0.44	0.015	0.031	71,550	132,700	18.0	36.0	6.0

Heat 498 was kept cool until after the alloy additions, when it was heated to a good pouring temperature. Heat 499 attained its maximum temperature just before the alloy additions. Other conditions were as nearly as possible the same. Both were given a double normalizing treatment at 1650° F. for the first and 1500° F. for the second treatment.

GENERAL THEORY

Although the data collected are much too meager to allow a detailed explanation of the phenomena that occur in deoxidation and inclusion formation, certain factors are so consistent and obvious that a tentative theory can be advanced. All of the facts so far cited point definitely to the great importance of iron and manganese oxides in the inclusions. Iron oxide, undoubtedly, is the more important of the two. The addition of aluminum to steel tends to eliminate the iron oxide. A low-carbon steel will be higher in iron oxide before deoxidation than a high-carbon steel. Adding iron oxide just previous to deoxidation causes the steel to contain much more iron oxide than equilibrium conditions would permit. Adding the manganese before the silicon causes the formation of manganese oxide, which in turn apparently causes the inclusions to be richer in basic oxides. Increasing the temperature previous to deoxidation causes the steel to carry more oxygen for the same carbon content.

In the ductile steels, there are the globular and the angular or crystal-line inclusions. The globular inclusions obviously were precipitated as liquids in a liquid medium; in other words, before the steel solidified. They retain their globular shape either because they solidified after the steel and were forced to retain their shape or because they did not crystallize but cooled to a glass. The angular inclusions, such as are shown in

Fig. 8 were precipitated as either liquid or solid in a liquid medium, but in any case, solidified as a crystalline material while the steel was still molten and, therefore, were able to assume their natural crystal shape. This type of inclusion is comparatively rare and has only been found in steels containing well over 1 per cent of manganese, and then only when the ductility is somewhat low. The explanation advanced for this is that in steels of this manganese content the sulfide consists principally of manganese sulfide, which has a melting point above that of steel. These sulfides, therefore, will crystallize before the steel freezes unless there are sufficient iron and manganese oxides present as such or as silicates to flux them and reduce the melting point.

The globular inclusions occur either as dark colored silicates, light

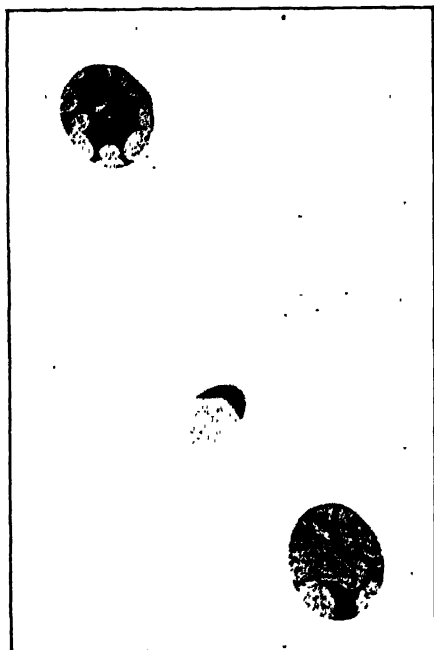


FIG. 23.—EXAMPLE OF DUPLEX INCLUSIONS IN 24-IN. CAST-STEEL RAM. $\times 400$.

colored sulfides, or as duplex inclusions containing both. Some excellent examples of the duplex inclusions are shown in Fig. 23. One large globule contains a large proportion of silicate with a small amount of sulfide, while another large one consists mainly of sulfide. Iron-manganese silicates and iron-manganese sulfides are miscible in the molten condition but separate on solidification. It is reasonable to suppose, however, that the sulfide is a saturated solid solution of iron-manganese silicate, while the silicate is a saturated solid solution of sulfide.

In the steels of low ductility, the inclusions that form part of the eutectic are of one constituent, which appears to be sulfide. The clusters of small dustlike particles, which are usually referred to as alumina, are believed to be aluminum silicate. There is SiO_2 somewhere, and if it is not with the sulfides, it must be with the alumina.

But why do the sulfides sometimes form globular inclusions, which are comparatively harmless to steel, and at other times form a network enveloping the primary crystals to the great detriment of ductility? It has been demonstrated that the quantity of iron oxide and manganese oxide present is the influence that controls the form that the sulfides will take. If there is sufficient iron oxide present, the sulfides will precipitate as the steel begins to freeze, while in the com-

parative absence of iron oxide the solubility of the sulfides is increased to such an extent that they separate only as a eutectic with the last steel to freeze.

When aluminum is added to steel, it first reduces iron oxide. If it reduces enough of it, the sulfide inclusions will be changed from the globular to the eutectic type, and the globular iron-manganese silicates to the refractory aluminum silicates. If there is a large quantity of iron oxide present, or only a small addition of aluminum is made, enough iron oxide will remain to precipitate the sulfides and the steel will not suffer in ductility. If iron oxide is added to steel which has already been treated with sufficient aluminum to change the sulfides to the eutectic type, the sulfides again take the globular shape, as shown in Fig. 9. But in such a case, the iron-manganese silicates are almost absent.

As may be seen in Fig. 7, a powerful deoxidizer, such as calcium silicide, has the same tendency as aluminum to cause low ductility through its indirect effect on the sulfides. A high-carbon content has a like tendency. In short, any condition that will lower the iron oxide content sufficiently will set the stage for low ductility. The obvious remedy is to maintain a proper amount of iron oxide by any method that will attain this end. Such a remedy has worked successfully in repeated tests.

SUMMARY

1. There is a direct relationship between the character and distribution of inclusions in cast steel and the ductility of such steels.
2. The globular type of inclusion scattered haphazardly through the steel has the minimum effect on the physical properties.
3. The eutectic type which forms a network in the steel causes the steel to rupture after slight plastic flow with resultant low ductility.
4. The variations in quantity of inclusions ordinarily found in steel have almost no effect on the physical properties.
5. The normal inclusion-forming material of steel is soluble in the molten state and precipitates as inclusions at the time of solidification.
6. If the iron oxide content of the steel is high, the inclusions will precipitate at the beginning of solidification and will exist as globules of silicates and sulfides, and the steel will have good ductility.
7. If the iron oxide content of the steel is too low, the solubility of the sulfides is increased to such an extent that they precipitate as a eutectic with the last steel to freeze. The ductility of such steel will be low.

ACKNOWLEDGMENT

The authors wish to express their appreciation for the cooperation, encouragement and kindly criticism of Mr. W. C. Hamilton, Director of Research, and to Mr. E. H. Burkart, who actively participated in the collection of data.

DISCUSSION

(F. M. Becket presiding)

G. F. Comstock, Niagara Falls, N. Y. (written discussion).—This paper seems to offer some entirely new ideas regarding the deoxidation of steel and the subject of inclusions. Moreover, the evidence submitted supports those ideas effectively, at least as applied to cast steel, and there seems to be no possible escape from many of the authors' conclusions.

The more qualitative metallographic methods for the study of inclusions should be brought back into favor by this work, as contrasted with the recently emphasized analytical methods or numerical counts, since it is so well demonstrated here that the arrangement of the particles is of the greatest practical importance rather than the total amount of nonmetallic matter present.

Although it is stated at the beginning of the paper that the conclusions apply only to cast steel, it would be well to emphasize this point more at the end, especially in connection with the final sentence of the "summary." In spite of the certainty that sulfide inclusions in the so-called "eutectic" form decrease the ductility of cast steel, it is almost equally certain from general experience that this does not hold true for all steel, since rolling or forging so alters the arrangement of the fine inclusions that they are no more harmful than those present originally as globules in the other type of steel. It has been shown many times that segregated alumina inclusions, especially when rolled out into streaks, were responsible for failures in drastically cold-worked steel and in hardened steel, so that it must not be concluded that alumina is generally harmless in steel simply because it is not found to be responsible for low ductility in castings.

In contemplating the broader aspects of the authors' theory that all inclusions, sulfides, silicates, and oxides, except alumina, are soluble in liquid steel, it would seem that the effect of temperature is of more importance than is recognized in the paper. The authors claim that holding steel in the ladle for inclusions to rise is not useful, since the inclusions are then all in solution. Nevertheless, they state that the solubility of the inclusions varies with the temperature. They do not give any temperatures of their steels, but it may be assumed as practically certain that their steels, to be used for small castings, were hotter than most steel which is made in larger heats for pouring into a smaller number of larger ingots. Is it not possible then that in spite of the authors' findings that inclusions are not eliminated in the ladle in their hot steel, yet in steel held at a lower temperature, for pouring into large ingots, inclusions may be formed and eliminated in the ladle as is now generally believed? Further work seems to be required on steel at definitely known temperatures before the authors' ideas along this line can be accepted as applicable to all steel. It is impossible, for instance, to explain by their theory the well established fact that steel deoxidized by ferrosilicon in the ingot mold is so much dirtier than similar steel deoxidized by the same substance in the ladle.

It would be very difficult, however, to reconcile the authors' results with the idea of *cleaning* the steel by deoxidizing additions in the furnace. Surely inclusions could hardly be eliminated at furnace temperatures in view of the facts now brought out. About the only advantage of deoxidation in the furnace as compared with deoxidation in the ladle would seem to be the longer period of action for the former practice, with consequent better opportunity for diffusion and more thorough decomposition of iron oxide.

At least in hot steel for castings, this work indicates that it is probably useless to try to form large inclusions in the ladle, so that they will rise easily to the slag.

The authors show, however, that larger inclusions are found in larger castings because the inclusions have a better opportunity to coalesce during slow cooling. In sand castings of ordinary size, it might well be too late then for their elimination, but this would not necessarily be the case in a large ingot. Even according to the authors' theory of formation of inclusions only in the mold, it would still be advantageous to form a more fluid type of inclusion in a large ingot, as by the use of titanium for instance, because such inclusions would have a greater tendency to collect with the segregate and be eliminated with the top discard.

C. E. SIMS and G. A. LILLIEQVIST (written discussion).—Mr. Comstock's criticisms are well taken, but there seems to be no serious conflict between his views and the theories advanced.

It is well, indeed, to place especial emphasis on the fact that the findings regarding ductility apply to cast steel and not necessarily to rolled or forged steel. Since this paper was written, convincing evidence has been obtained that the flow of the steel in drastic forging or rolling so rearranges and breaks up the inclusions that their effect is apt to be entirely different. I have in mind two steels of the same composition that differed greatly in ductility in the as-cast condition but which showed no such difference after drastic forging.

Reference was made to failures in drastically cold-worked steel and hardened steel due to rolled-out streaks of alumina inclusions. I should like to know whether these failures were thought to be caused by low ductility or fatigue. We did not intend to discuss fatigue, but numerous fatigue failures in rolled steel products have been traced to rolled-out streaks of inclusions. However, these rolled-out streaks of inclusions were not all alumina, and we believe that any inclusion that will crush to fragments during rolling is just as dangerous from an endurance standpoint as alumina or aluminum silicate.

Mr. Comstock suggests that not enough importance has been attached to the influence of temperature on the solubility of inclusion-forming material and that the possibility of elimination of inclusions in the ladle due to cooling of the metal has been overlooked. In the second paragraph of page 166 of the paper, it is pointed out that the "solubility of the nonmetallics is probably limited and varies with the temperature." As the steel cools toward the freezing point, the solubility is decreased and a few inclusions are formed. In the last paragraph of that page is the notation, "Any amount over the saturation point seems to be quickly eliminated from the bath." Therefore, it seems certain that as the temperature of steel in the ladle decreases, some inclusions will be precipitated and eliminated. However, the quantity of true inclusions lost in this manner is so small as to be relatively unimportant and apparently does not produce clean steel.

In regard to the observation that steel deoxidized in the ingot mold with ferro-silicon is so much dirtier than similar steel deoxidized with the same material in the ladle, is it not possible that a quantity of ferrous silicate in excess of the saturation point is formed in either case but that when formed in the ingot there is no chance for the escape of the excess?

The data on which conclusions were drawn were not obtained from unusually hot steel. Temperature measurements have been made on many of the heats with an optical pyrometer, but we hesitate to give any figures as correct temperatures. The average heats from the experimental induction furnace are about 2900° F., while the heats called "hot" heats are close to 3000° F. In the shop, bottom-pour ladles are used and it is not necessary to have the steel so hot as when hand shanks are used. Usually, a small skull is left in the ladle. For instance, in the heat in which the series of different sized sections were poured, and which is described on page 164, the temperature was between 2800° and 2850° F. at the tap.

There seems to be a slight misunderstanding regarding the explanation of the manner in which large inclusions are formed when the steel freezes slowly. As described on page 166, second paragraph, the word coalesce is not used and it is believed that there is very little opportunity for the coalescence of inclusions during solidification. The steel is then too sluggish and the mobility too low. As the steel cools and the solubility decreases, the nonmetallics are progressively precipitated on inclusions already formed in preference to forming new ones. There is, thus, a race between rate of precipitation and rate of diffusion. In rapid cooling, there is little time for diffusion; and the result is small and numerous inclusions.

A. B. KINZEL and W. CRAFTS, New York, N. Y. (written discussion).—The work reported by Sims and Lillieqvist is certainly timely and of great interest, not only to the manufacturer of steel castings but also to the producer of steel ingots. That the network caused by aluminum is responsible for low ductility in castings has again been effectively shown. The solubility of the aluminum-bearing sulfides and silicates has been beautifully demonstrated, together with the effect of mass on the size of the inclusions. That the sulfide constituent is soluble in molten steel is believed to be generally true in this class of steel, but the range of solubility of silicates is believed to be dependent to a great degree on their composition. It is probable that iron silicates are least soluble and that manganese silicates are slightly more soluble with a large proportion of the silicates still remaining insoluble in the molten metal. From our experience, we would consider the 0.27 carbon heat with 1 lb. per ton of aluminum, which was cast in varying sections, to represent almost complete solubility of both sulfides and silicates. In this grade of steel, the group of closely arranged silicate inclusions, which is the first evidence of large silicate solubility, becomes evident with an aluminum addition of about 10 oz. Al per ton. In order to work out these relations, it is necessary to have quantitative data and it is unfortunate that the authors did not see fit to include approximate solubility diagrams. The hypothesis presented by the authors is particularly interesting in the light of the successful initial deoxidation of steel by means of silicomanganese. Were these silicates highly soluble, such practice would not be efficacious. However, it is our opinion that if the authors had worked out the diagrams, the solubilities would be shown to be such that the theory of initial deoxidation would not be at variance with the authors' findings.

The importance of the type rather than the amount of inclusions has been strongly emphasized and we fully concur with the conclusions of the authors. The method of treating the metal with ore is of great interest. That the castings are free from porosity after this treatment would indicate a stabilization of nonmetallics which is of major importance.

The ratio between soluble sulfides and oxides appears to be the determining factor in the type of inclusion produced. This may be controlled in a number of ways to produce ductile castings by utilizing the relative oxide and sulfide tendencies of various deoxidizers. Very successful steel castings have been produced by the use of zirconium, and it appears that the amount of this metal added is less critical than that of aluminum in readily producing the desired type of inclusions. The low ductility reported from the use of calcium-silicon is not confirmed by our experience, as calcium-silicon does not readily modify the sulfides and has been found to be most effective in producing sound castings with good ductility.

B. M. LARSEN, Kearny, N. J.—I happen to know some details of some studies of inclusions in ball-bearing race steel made in an electric furnace in which the small cup-test samples from the ladle showed the presence of numbers of very small inclusions under high magnification, with no very big inclusions, while corresponding samples from ingots showed much larger inclusions, the size of which increased with

the size of the ingot. Whether or not these inclusions were all or partly formed by precipitation from the liquid metal before solidification began, at least they did seem to grow during the period of freezing, as shown by Mr. Sims.

On the other hand, I think there is circumstantial evidence to indicate that precipitation of inclusions does take place in the liquid steel before pouring into molds. Probably Mr. Sims will agree with me that this occurs to some extent, at least. I remember that once when some narrow test ingots were cast in sand molds from small hand ladles of electric-furnace low-manganese alloy steel to which manganese and silicon had been added only a few seconds before, we found just beneath the surface of a horizontal shelf near the top of the bars, very large manganese silicate inclusions as big as 1 to 2 mm. in diameter, which were rising rapidly from the metal just after it entered the mold, but were caught in the surface crust of iron. In a matter of seconds of longer holding the metal in the ladle, these would probably have risen to the surface and been absorbed by the slag; I think they would not have attained such large sizes during the freezing of these 1 to 1½-in. bars.

The rising velocity of inclusions of a given density should from Stokes' law vary with the square of the diameter of any particle. Plotting the rising rate for a given size of inclusion, according to Stokes' law, gives a curve with a very sharp rise in a small range of decreasing diameters. This means that the larger particles quickly rise out of the metal, having the smaller particles of about the same size range in all heats of commercial steel after they have been deoxidized and held in the ladle, even though the time of holding the ladle varies widely.

During the freezing of such steel, a certain amount of FeO and possibly MnO and SiO₂ are precipitated, and these may help to flux together the residual suspended matter into larger final particles, especially in very large masses of metal. At least, this is a possible explanation of the results obtained by Messrs. Sims and Lillieqvist. Their data show nicely the predominant effect of the form of the sulfide inclusions, and apparently that their distribution and arrangement is modified by the presence of MnO or FeO as well as by manganese alone. The need for very careful laboratory study of the combined effect of oxygen, manganese and sulfur is clearly indicated by this paper.

There seems to be no point in arguing at length the question as to whether inclusions are soluble or insoluble in liquid steel. They are not definitely either one or the other, of course, but have certain solubility limits which may vary. We know, for example, that iron sulfide is completely miscible in liquid steel, but only very slightly soluble in solid steel, with a eutectic point at 980° C., that manganese sulfide is much less soluble in the liquid metal but is soluble in amounts much larger than those present in all commercial steels, and probably insoluble in the solid metal; that FeO has an appreciable but limited solubility in both liquid and solid iron, with MnO and SiO₂, etc., having still smaller but unknown values. It has been shown by Dr. Herty and others that at the lower temperatures existing in pig iron after transfer of the ladle from the blast furnace to the open hearth, part of the sulfur is precipitated, because the solubility limit is small at these lower temperatures. With ordinary amounts of sulfur and manganese in steel, the latter is beginning to freeze before this solubility line is passed, so that the sulfide inclusions ordinarily are precipitated during freezing or in the solid metal.

As far as the data on the effects of sulfides, oxides and silicates on each other's solubility limits are concerned, we know almost nothing at all.

As we slowly accumulate data on the distribution coefficients of oxygen, sulfur, manganese, silicon, etc., between slag and metal phases, we shall be able gradually to treat this subject in a more rational and scientific manner, and perhaps ultimately obtain a physical-chemical picture of the subject matter which is under discussion,

but in the meantime I think that Mr. Sims' method of approach is probably very much the most logical one. We do not have enough fundamental data to be able to figure out the problem rationally, so we can hardly work out certain of these practical problems by any other than the empirical method.

R. S. DEAN, Washington, D. C.—One factor seems to have been completely overlooked in the consideration of bringing inclusions to the surface of steel; so large a factor, it seems to me, as to push all the other considerations into the background. I notice continual reference to Stokes' law for the rising rate of inclusions. What would be the result of its application to a flotation cell? Here there is a set of conditions with gas evolved in the metal. I do not think there is any doubt that the thing that causes the inclusion to rise is the ability to attach a gas bubble. If there is an inclusion with a great deal of manganese oxide or iron oxide, gas is formed by their reaction with the carbon in the iron, and attaches to the particle and up it goes. That balloon effect, it seems to me, is very largely responsible in removing the inclusions from a steel bath, and it seems to have been largely neglected.

R. A. BULL, Chicago, Ill. (written discussion).—In papers previously published on inclusions in steel, some conclusions have been based disproportionately on theoretical considerations, resulting in misunderstandings by certain purchasers. Some experimenters have presented interesting data from which they have made deductions on the premise that steel that is dirty, as gaged by the total amount of inclusions observed at a given magnification, is *ipso facto* incapable of enduring satisfactorily the severe stresses to which many structural parts are subjected.

Not a few investigators have confidently looked for improvement in the cleanliness of steel, to follow innovations in melting equipment that seemed to some persons to offer the best opportunities for excluding the impurities often termed sonims. But steelmakers appear generally to have found no definite relationship that can be established between steelmaking process and the total amount of sonims.

A baffling feature of the study of inclusions lies in the repeated demonstration that conventional physical tests fail to disclose the effect of impurities of the kind discussed in this paper. By this is meant the absence of a relationship between relatively clean steel and good physical properties on the one hand and steel rather heavily loaded with inclusions of the kind called sonims and poor physical properties on the other hand. Many who have conscientiously tried to ascertain a relationship between cleanliness and physical performance have been puzzled to discover no such connection, when a satisfactorily large number of specimens of similar kinds of steel is made the basis for comparison.

It becomes illuminating and highly suggestive to those who have been concerned with this problem, to be advised of the results of work done by Sims and Lillieqvist. While they submit their data only as partial evidence, justifying further study, they present information that may lead to future definite conclusions regarding the effect of inclusions, not so much in respect to total amount as to shape, constituents, causes and remedies.

A study of the text and illustrations appears to justify the tentative conclusions reached by the authors. The relationship between the shape of the inclusion and its effect seems to have been fairly well established; likewise the relationship between the shape of the inclusion and the function of oxides in influencing the behavior of aluminum, added late to the steel. It is to be hoped that the work done in the laboratory of the American Steel Foundries will prompt further investigations along the same line by other steel companies, and that ultimately, even if we never learn how to eliminate inclusions, we may find out how to regulate their forms, and by this or/and some other means, to make them innocuous.

Dr. John A. Mathews' viewpoint of the matter^a probably is held by the majority of practical steelmakers who have conscientiously tried to determine definitely the causes and effects of inclusions. In the discussion mentioned Dr. Mathews commented on the fact that some engineers have become so inclusion minded that they look on sonims as the root of all dynamic evil, and attach photographs to purchase specifications, showing what they expect their steel to resemble. As several researchers have pointed out, inclusions of the kind discussed in this paper are the normal result of the introduction of degasifiers.

Where conditions exist either in the metal or in the transfer of it to the mold, or in the mold itself, which are certain to produce gas when contact between the mold and the liquid metal is made, and where consequently it is desirable (as in steel foundry practice) to exclude all such gas from the metal before it freezes, one must, apparently, resort to the late addition of one or more degasifiers. The problem lies in the skilful introduction of such degasifiers in a way to prevent injury to any valuable property of the steel. It seems visionary to expect that this feat can be accomplished in the steel foundry, where, very often, important considerations justify the use of green-sand molds, without the formation of inclusions as the result of reactions essential for the major purpose. If, now, we may learn how to control the formation, characteristics, and interrelationships of these inclusions in a manner to prevent deterioration of any important property, we will have reached a stage of progress commanding respect. It is quite conceivable that this result may be attended by an abhorrence for sonims, only as they may be observed to have undesirable characteristics, and without especial regard for their total amount. Inclusions of a certain kind might even be found desirable, as evidence of proper treatment of the metal for the special purpose under consideration.

Sims and Lillieqvist may have materially assisted us who are steel foundrymen to attain our objective. The data presented in their interesting paper merit our serious consideration, and should result in numerous experiments for the purpose of confirmation.

C. H. HERTY, JR., Pittsburgh, Pa. (written discussion).—After carefully reading over this paper, I am much impressed by the fact that the authors pay no attention to two well-known facts: (1) that coalescence of nonmetallic inclusions has been experimentally demonstrated, and (2) that nonmetallic inclusions can be eliminated by allowing steel to stand for a sufficient length of time after deoxidation, the length of time necessarily depending upon the size of the nonmetallic particles. In conjunction with Dr. G. R. Fitterer and other members of the staff of the U. S. Bureau of Mines, I have made an extended series of tests dealing with deoxidation of steel with silicon, manganese and aluminum. The findings of these investigations have been reported in technical papers and as cooperative bulletins of the Metallurgical Advisory Board of the Carnegie Institute of Technology and as reports of the U. S. Bureau of Mines. In *Cooperative Bull.* 36, Fig. 13 shows the coalescence of silicate particles in the center of an ingot and large particles of silica in the chilled crystals of the ingot. These particles in the chilled crystals must have been present in the liquid steel in the same size as in solid steel, and the larger particles in the center of the ingot are due solely to coalescence and to fluxing of FeO by the silica particles. These phenomena have also been demonstrated in U. S. Bureau of Mines *Tech. Paper* 492, and in the *Transactions* of the American Society for Steel Treating (1928). Similar coalescence of inclusions of other compositions have been shown in other publications.

The elimination of inclusions by coalescence with subsequent rising of inclusions in the steel bath has been shown in *Cooperative Bull.* 38, and Bureau of Mines *Tech.*

^a J. A. Mathews: *Trans. A. I. M. E.* (1931) 95, Iron and Steel Div., 188.

Paper 492. An example of the elimination of silicates after deoxidation with silicon in the open-hearth furnace is given on page 28 of the latter paper as follows:

Time	Silicates, Per Cent	Remarks	Time	Silicates, Per Cent	Remarks
2:24		10 per cent silicon pig added to bath	2:48	0.060	
			3:00	0.038	
2:28	0.055		3:10	0.026	
2:30	0.063		3:20	0.003	
2:34	0.082				

From the general nature of the loss of ductility following the use of aluminum together with the photomicrographs shown in the paper, it would appear that sulfur and its distribution in the steel is of primary importance. There is no question but that sulfides are soluble in liquid steel. This has been shown experimentally many times. The effect of aluminum on the distribution of these sulfides would appear to be the major factor in the disposition of the inclusions in the finished steel. It is possible that aluminum in solution changes the solubility of the sulfides to such an extent that they do not precipitate until the very last bit of liquid metal at any given point has solidified. These sulfides would then be found directly in the grain boundaries as films or as tiny particles which had no time to coalesce. A more extensive discussion of this question is to be given in a paper before the American Foundrymen's Association in May, 1932, and no further reference will be made at this point. It is possible that the iron ore addition to the aluminum-treated steel in Table 3 resulted in a complete elimination of aluminum with the resultant change in the solubility of the sulfides.

The authors' conclusion that the iron oxide content of the steel controls the solubility of the sulfides would appear untenable because high silicon additions will deoxidize to the same extent that some lower aluminum addition will. Therefore, it could hardly be the variation of iron oxide in the liquid steel, but more probably the presence of aluminum in solution, which causes the variation in the type of inclusion in the casting.

I believe that the authors are correct in their statement that "if the steel can be made sulfur free, a large portion of the inclusions would be automatically eliminated." It would appear that research on this particular question would rapidly pay dividends to the manufacturers of steel castings.

L. E. GRANT, Milwaukee, Wis. (written discussion).—We have read with considerable interest this valuable contribution to the solution of the puzzling problem of low ductility in steel castings. While some of the suggestions made will undoubtedly not be universally accepted, a frank discussion of the whole question of low ductility is certain to be beneficial. We were especially interested in the authors' statement that they were able to predict ductility from an examination of the unetched specimen on the microscope. Our experience has been similar in a limited way. We have not attempted to predict the physicals, as we had not correlated our observations to such a degree of precision, but we have been able to predict in many cases that the ductility would be low. We have observed that when the inclusions are present in V-shaped or Y-shaped forms the ductility is likely to be abnormally low. Such groups are formed by the inclusions collecting at the junction of primary grains. Fig. 24 shows one of the worst cases of this type we have seen. This specimen was from a failed locomotive crosshead. The physical properties were as follows: yield point,

43,000 lb. per sq. in.; tensile strength, 76,600 lb. per sq. in.; elongation in 2 in., 13.0 per cent; reduction in area, 15.4 per cent. The composition was: carbon, 0.35 per cent; manganese, 0.65; phosphorous, 0.020; sulfur, 0.041.

Another factor which we believe to have a significant influence on ductility is grain size. The authors may not have encountered any marked variation in this factor as undoubtedly their steels were all properly heat-treated. Some railroad castings are furnished by small foundries without any metallurgical control and the heat treating is improperly done. As a result it is not uncommon in our laboratory to find steel castings with excessively coarse grain size. The intermediate manganese steels are particularly bad offenders in this respect. Such specimens have low ductility regardless of the type of inclusions. We do not doubt, however, that this factor acts independently of the inclusions, so that a coarse-grained steel with chained inclusions would have a lower ductility than if only the rounded type of inclusions was present.!

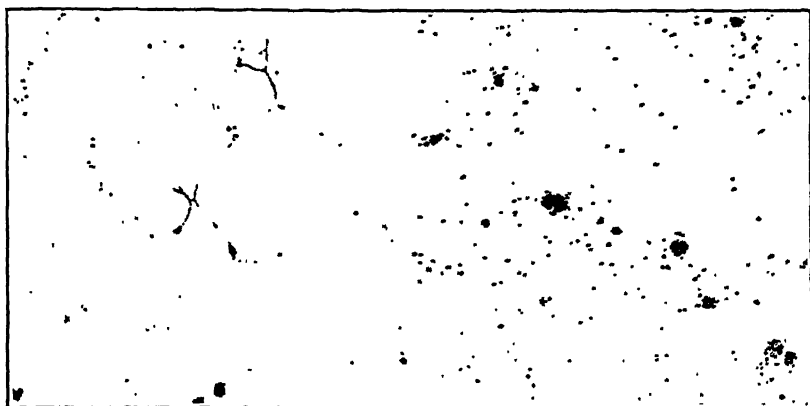


FIG. 24.

FIG. 25.

In support of their theory of the solubility of inclusions the authors report that variation in the quantity of inclusions is not great. Our experience has been contrary to this. In the examination of both large and small castings from many different foundries we have found a wide variation in the quantity of inclusions. Generally speaking, we would classify steel such as shown in Fig. 10 as moderately clean. Fig. 25 shows our conception of dirty steel. Cast steel of about this same character is not as uncommon in our laboratory as we could wish. Nevertheless we believe the evidence presented indicates some solubility of the inclusions in the liquid steel. But acceptance of this theory raises a difficult question when it is applied to large ingots, as it indicates that extremely large inclusions must be present. Ingot studies reported in the literature do not confirm this and in our examination of moderately large forgings we have not found large inclusions consistently. In fact, the largest inclusion we have seen was found in a small ingot about 4 in. square, weighing less than 100 lb. Evidently factors other than solubility are involved.

If other steel foundries can consistently overcome the low ductility, which so often accompanies the use of aluminum, by the application of the information set forth in this paper the authors will have made a notable contribution to the art of steelmaking.

J. DESCHAMPS, Letchworth, Herts, England (written discussion).—In our company we are employing the surface-blown acid-lined converter for the production of

the steel we require for our steel foundry. Our converters are of about $2\frac{1}{2}$ tons capacity and the metallic charge in our cupolas consists of about 70 per cent selected steel scrap and 30 per cent low-phosphorus high-silicon hematite pig iron.

We also operate a basic-lined electric furnace and it has been our experience that although the steel obtained from our electric furnace contains much less sulfur and phosphorus and is freer from oxides than steel from the converter plant, we have always obtained better physical results from test pieces made with the converter steel than from test pieces made from the basic electric steel.

Repeated microscopic tests have regularly shown that the amount of nonmetallic inclusions in our converter steel is nearly always considerably greater than that found in properly made basic electric steel, and until we read the lucid explanation by Sims and Lillieqvist of the effect of iron oxide on the arrangement of these nonmetallic inclusions in the metal, we could not understand why so much better results could be obtained from the converter steel, which appeared to be inferior to the basic electric steel both from the point of view of chemical purity and of the amount of nonmetallic inclusions present in the metal.

When proper care is taken, we obtain from our converter metal extremely good results. For instance, with a metal containing about 0.35 per cent C, 0.7 per cent Mn, 0.35 per cent Si, 0.04 per cent S and 0.06 per cent P, a test piece subjected to normal annealing treatment gives us about 85,000 lb. tensile coupled with 22 per cent elongation on 2 in., and a cold bend without fracture of 180° .

We have never been able to obtain such results, particularly a cold bend of 180° without fracture, with a basic electric steel, and this leads us to express the opinion that there should still be a great future for converter steel, in the manufacture of which such conditions arise as are favorable to the presence of a certain amount of unreduced iron oxide which, according to the findings of Sims and Lillieqvist promotes a better arrangement of the nonmetallic inclusions in the metal.

We notice that the paper does not mention the converter process. We are well aware that this process has lately fallen into disrepute, principally, we believe, owing to poor operating methods, and we would very much like to have the authors' opinion on the remarks in our discussion.

We would like to mention that the low sulfur content we obtain in our converter steel, notwithstanding the high proportion of steel scrap used in the cupola charge, is due to the fact that the metal issuing from the cupola is carefully desulfurized with soda ash prior to being blown in the converters.

F. G. NORRIS, Middletown, Ohio (written discussion).—Inclusions are present because the amount of nonmetallic phase is in excess of its solubility in the steel. Some inclusions, which may be termed primary inclusions, are precipitated immediately after they are formed and, for purposes of discussion, may be considered as never having been in solution. Keeping constant the amount of nonmetallic substance in the system, any change which decreases the solubility of the inclusions in the metal will supersaturate the metal and will thus be a potential cause for the formation of additional (secondary) inclusions. Whether the inclusions actually precipitate or remain in supersaturated solution depends on a number of factors beyond the scope of this discussion.

Apparently what we have termed primary inclusions are entirely disregarded by the authors—perhaps because they doubt the existence of this type of inclusions. The discussion near the top of page 166, which deals with secondary inclusions, may be expanded in some detail.

Secondary inclusions are those which have once been in solution and which precipitate because the solubility relations change with decreasing temperature, the total

amount of inclusion material in the system remaining constant. Secondary inclusions may be classified according to the change that makes their precipitation possible:

1. Inclusions that precipitate from liquid steel because of the decrease in solubility in the liquid with decrease in temperature.

2. Inclusions that precipitate from liquid steel because of the increase in concentration in the liquid caused by segregation (freezing of steel with lower inclusions in the solid than in the melt).

3. Inclusions that precipitate from solid steel because of the decrease in solubility with change from liquid to solid.

4. Inclusions that precipitate from solid steel because of decrease in solubility in the solid with decrease in temperature.

It is immaterial whether the precipitated inclusions are liquid or solid, this depending on the composition of the inclusions being considered. In the above classification changes in solubility due to allotropic changes are not considered, but may have an effect in case of some types of inclusions.

The importance and relative amounts of inclusions from the various sources considered depend entirely on these solubility relations. Thus, according to the usual equilibrium diagram, primary inclusions of FeO are never present in commercial steel. However, there is reason to believe that other inclusions exist chiefly as primary inclusions and that their presence as secondary inclusions is negligible.

Only inclusions that are present in the liquid before solidification starts, that is in the ladle, will be subject to elimination by rising through the liquid. Thus it is apparent that secondary inclusions listed in classes 2, 3 and 4 do not have a chance to be eliminated in this manner.

TABLE 5.—*Elimination of Oxides*

FROM OPEN-HEARTH HEATS

Heat	A	B	C
O ₂ furnace sample (aluminum method), per cent	0.062	0.095	0.060
Si Mn added, lb.....	1000	1900	2700
O ₂ before teeming (vacuum fusion), per cent.	0.056	0.035	0.018
O ₂ 5th ingot (residue method), per cent.....	0.019	0.014	0.012
O ₂ 19th ingot (residue method), per cent.....	0.021	0.016	0.015

FROM 500-LB. AJAX HEAT

Time	Carbon, Per Cent	Manganese, Per Cent	Silicon, Per Cent	Oxygen (Al Method), Per Cent
4:57 p. m.	0.02	0.051		0.052
5:00		added silicomanganese		
5:10		0.36	0.052	0.021
5:20	0.04	0.36	0.049	0.016

As we understand the third paragraph on page 162, this section pertains only to inclusions completely soluble in liquid steel. However, this limitation is not clearly brought out and may be a source of confusion in the mind of the reader, especially in regard to the statement that results of attempting to float out inclusions have been universally disappointing. When primary inclusions are involved the results are promising and are at least qualitatively as would be expected from Stokes' law.

Rather complete evidence of this elimination has been published at various times by Herty, the most recent being in the *Transactions* of the American Society for Steel Treating. Zieler⁹ reports evidence of elimination of inclusions due to floating out. The results of Bardenheuer and Ranfft¹⁰ indicate that inclusions were rising in the ladle although the inclusion content of their steel was low. Further elimination of the inclusions due to floating out is shown in Table 5. These are exceptions (and there may be more) to the universally disappointing results which the authors mention.

In regard to conclusion 5, we agree that all inclusions are slightly soluble in liquid steel and that some inclusions may be completely soluble in liquid steel. However, we would like to ask if the authors mean that inclusions such as SiO_2 and Al_2O_3 in amounts of 0.03 to 0.05 per cent are completely soluble in the liquid steel and did not precipitate until the time of solidification.

R. B. SOSMAN, Kearny, N. J. (written discussion).—The phenomena of flocculation and dispersion of these inclusions are of considerable interest. In discussing this subject at the public session of the Metallurgical Advisory Board in Pittsburgh, Oct. 17, 1930, I stated that there was no reason to expect any influence of one inclusion upon another when they were separated by a distance of more than a few thousandths of a millimeter. This statement was made in the face of a polished section shown by Dr. Herty on which there was a large globular inclusion surrounded by a ring of small satellites, the inference being that the large inclusion was drawing in and absorbing the small ones. The natural assumption regarding rising liquid inclusions has been that the only process influencing their size is their coalescence into larger units. The logical deduction from Dr. Herty's photograph, on the other hand, is that the small satellites are on their way out from the central globule, not on their way in. Some light is likely to be thrown on this problem by the investigations of Rashevsky, who is presenting a paper at the Cambridge meeting of the American Physical Society on Feb. 27, on Spontaneous Dispersion of Small Liquid Systems Which Are the Seat of Physicochemical Reactions. Rashevsky is principally interested in the applications to biological phenomena, but the principles are equally applicable in metallurgy. Generalizing his earlier deductions, which involved the surface tension between a liquid drop and the surrounding medium, Rashevsky finds now that any suspended drop in which a chemical reaction is occurring has an upper limit of size, and if larger than this, it is dispersed. It may be that the metallurgist studying the rise of inclusions will have to distinguish between a liquid inclusion in internal equilibrium and one in which a reaction is occurring. The latter may be dispersing itself instead of coalescing with others to form larger drops.

W. I. CANTLEY, Bethlehem, Pa. (written discussion).—From the railroad's point of view, my discussion of this paper concerns principally the practical aspect of the findings rather than the technical or theoretical aspects. Although considerable work has been done by various investigators on the effect and characteristics of inclusions in steel, most of such work has been of a highly technical order and of such character as to be difficult of interpretation in terms that would convey to the layman the significance of the results with relation to their effect on the more common properties of the metals.

In the paper under discussion, the authors clearly demonstrate that a definite type of inclusion has a definite effect on the physical properties of the metal. The consistency of results obtained under repeated observations establishes beyond

⁹ Influence of Zr, Na, and Ca on Nonmetallic Inclusions in Steel. *Archiv. f. d. Eisenhüttenwesen* (December, 1931).

¹⁰ Change of Composition of Basic Steel in the Ladle. *Mitt. K. W. I. f. Eisenforsch. zu Dusseldorf* (1931) 13, 195-305.

reasonable doubt the accuracy of their conclusions and adds materially to the immediate practical value of their contributions.

As a user of large tonnages of various steel products, we are keenly appreciative of the points developed by Messrs. Sims and Lillieqvist in their work and believe that it will lead to a better understanding of a problem which has been rather obscure, and with the stimulation of effort which undoubtedly will follow on the part of other investigators we should expect an actual improvement in the quality of steel products.

It is of interest to note the evidence produced of the solubility of inclusions. The information developed is of considerable importance and if the theories advanced by the authors as a result of their investigation can be verified in fact it should have a far-reaching effect on steel-mill practice and definitely point the way to the production of "clean steel."

In paragraph 4 in the Summary, it is stated: "The variations in quantity of inclusions ordinarily found in steel have almost no effect on the physical properties." We presume that the term "physical properties" in this instance means only the tensile strength and ductility as determined by static test and also the Izod value. We particularly stress this distinction to avoid a possibility of literal interpretation of the statement.

G. F. STAMMLER, Bethlehem, Pa. (written discussion).—The results (especially those obtained from the steels to which no aluminum was added) reported in the paper by Sims and Lillieqvist check well with other investigators. The writer, however, does not agree that the amounts of inclusions found in a steel are dependent upon solubility of the inclusions, nor with other theories advanced, but is of the opinion that all liquid steels deoxidized with silicon and manganese contain a very small amount of inclusions and that the amount of silicate inclusions found in the solidified product is dependent upon the rate of solidification of the steel. He bases his conclusions on the following facts.

The first investigator to call attention to the distribution of silicate inclusions was J. H. S. Dickenson.¹¹ He found a central zone of silicate enrichment, the maximum silicate content of his ingots being in the lower central half. In the upper portion of the ingot, we find less silicate in the center but a slight enrichment between the middle and outside. The silicate content along the edge of the ingot showed a marked uniformity, the amounts found along the edge of one ingot showing the following percentages of inclusions: 0.022, 0.026, 0.026 and 0.022.

Later results by Dr. Herty and his associates at the Bureau of Mines Experimental Station, and other investigators, confirmed the findings of Mr. Dickenson.¹²

Since all the results show a uniformity in the amounts of inclusions found along the edge of the individual ingots, the writer believes this amount is representative of the inclusions in the steel as it leaves the ladle. The edge of the ingot is the steel which solidifies almost instantly, and the inclusions are at once entrapped and held by the steel. If several ingots show an average silicate-inclusion content of 0.018 per cent along the edge, the writer cannot conceive how there should be three times that amount in the center, due to "freezing out" or "coalescence." We therefore believe that the increased inclusions found in the center of the ingots are reaction products between metals and gases liberated during slow solidification.

¹¹ *Jnl. Iron and Steel Inst.* (1926) 113, 177.

¹² In *Bull.* 36, Physical Chemistry of Steel Making—Deoxidation with Silicon and the Formation of Ferrous-silicate Inclusions, pp. 47–48, they give their comments on the theory of inclusions advanced by others and their own conclusions.

Several papers have been presented, giving data on the solubility of gases in metals:¹³ and in all of the papers, the metals have been a single element. Steel, on the other hand, is a combination of metals in addition to carbides, sulfides, etc., and these compounds (chiefly the carbides) appear to have a controlling influence on the amount and composition of the gases dissolved by the steel.

Experiments, conducted in 1927 at the Hamilton Works of the Steel Company of Canada, on the gases given off by steels as they solidified in the ingots, showed that the gases consisted of carbon monoxide, hydrogen, carbon dioxide and nitrogen, but no free oxygen. These tests were conducted on steels of rimming grade, ranging from 0.05 to 0.22 C, and on killed steels ranging from 0.22 to 0.94 C. The high-carbon steels gave gases which contained a greater percentage of carbon dioxide than found in the rimmed steels, but the chief constituent of all the gases was carbon monoxide.

Later experiments by Messrs. Brace and Ziegler¹⁴ on *quickly solidified* tests showed that carbon monoxide was the chief gas extracted. They used melts of various carbon contents and the amounts of gas extracted varied with the carbon content of the metal. The gases obtained in their experiments were carbon monoxide and carbon dioxide, the former being greatly in excess. The vacuum fusion method would form these gases with oxides in the metal, but it seems unreasonable to believe that high-carbon steels and pig irons should contain more metallic oxides or uncombined oxygen gas than a low-carbon steel; so the writer has concluded that they contained more carbon monoxide, the amount varying with the carbon content of the metal.

Even with nitriding steels which contain 1.00 per cent Al, we see the effect of the solubility of gases in alloys of this type. This was demonstrated by casting two small ingots of this grade in a chilled steel mold and in a heated sand mold of the same inside dimensions. In the former, the steel was solidified very rapidly, preventing the liberation of much gas, and giving an ingot containing few inclusions and only a small pipe cavity. On the other hand, the ingot which solidified slowly contained twice the amount of inclusions, a pipe cavity which contained three times the volume of that in the chilled ingot, and also porous spots in the center of the lower portion of the ingot. Since aluminum reacts with dissolved oxygen and oxides of the metals (this property being utilized by Dr. Herty to determine oxides in molten steel), the gas liberated is not dissolved oxygen but is probably carbon monoxide, which is not reacted upon by the aluminum at tapping or pouring temperatures.

Since carbon monoxide is one of the chief gases dissolved by molten steel and its amount is apparently due to the carbon or carbide content of the metal, how does this gas have any effect on the formation of inclusions? With slow solidification, the carbon monoxide is liberated by the steel and some of the gas reacts with the elements in the metal (chiefly manganese, silicon and iron) causing the formation of their oxides, and the liberated carbon combines to form carbides. This is illustrated by the following equation, in which we show the first reaction with manganese: $\text{CO} + \text{Mn} = \text{MnO} + \text{C}$ and $\text{C} + 3\text{Fe} = \text{Fe}_3\text{C}$. As solidification proceeds from the outside to the center of the ingot, we find the maximum amount of oxides formed at the center where the metal solidified last. In the bottom half of the ingot, the metal becomes semiliquid much more quickly than in the upper half: and the oxides are thus entrapped in this portion to a greater degree than in the top half of the ingot.

¹³ V. H. Gottschalk and R. S. Dean: The Solubility of Gases in Metals. A. I. M. E. Preprint.

F. J. Norton and A. L. Marshall: The Degassing of Metals. A. I. M. E. Preprint.

O. W. Ellis: A Review of Work on Gases in Copper. A. I. M. E. Tech. Pub. 478.

¹⁴ Gases Extracted from Iron-carbon Alloys by Vacuum Melting. Trans. A. I. M. E. (1929) 84, Iron and Steel Div., 428.

In the upper half, there are thinner walls of the ingot molds, and with ingots of the sink-head type is the greatest cross-section of the ingot, in addition to the hot top which keeps the metal liquid for a longer time. Even though reactions between the carbon monoxide and the elements in the steel continue for a longer period, the fluid condition of the metal permits the oxides to escape into the hot top: especially as the oxides may be assisted by becoming attached to some of the escaping gas particles.

In the bessemer process we have almost a direct reversal of the formation of oxide which we believe takes place during the solidification of the steel in the ingot. In the blowing of bessemer metal, the first oxides formed are those of manganese, silicon and iron; chiefly the last, due to mass action, and there is an interchange between its oxygen and the two first-named elements. The silicon content of the hot metal is first reduced, then the manganese and lastly the carbon. In order to insure the oxidation of the manganese before the carbon oxidation, it is necessary either to add cold scrap to the converter or admit steam with the air. This is done to keep down the temperature, as carbon has the greater affinity for oxygen at the higher heat. In the solidification of the ingot occur the reverse of the conditions in blowing a bessemer heat; i.e., the metal as it leaves the ladle is at high temperature and contains dissolved carbon monoxide. The molten steel retains this gas when poured into the ingot mold but as the temperature is gradually decreased, the gas is slowly rejected by the metal. With lower temperatures, the elements manganese, silicon and iron (and aluminum if present) have a greater affinity for oxygen than carbon, causing the formation of their oxides and liberating carbon so that it can be taken up by the metals to form carbides.

This affinity of carbon for oxygen at higher temperatures is also shown in the vacuum fusion method. In this method, the oxides are reduced by means of the carbon of the crucible and high temperature to carbon monoxide, the gases are drawn off, and weighed or measured. Should the steel contain over 0.2 per cent Mn, some of the manganese vapors in the cooler part of the apparatus react with the carbon monoxide being drawn off and cause the formation of manganese oxide ($\text{CO} + \text{Mn} = \text{MnO} + \text{C}$) and give low results. Similar effects have been caused by the presence of aluminum vapors when the steel contained more than 0.3 per cent Al.¹⁵

The writer believes this theory (of reactions during solidification) also offers an explanation for the "segregation" of carbon in steels, as the "freezing out" of carbon-rich material fails to answer some questions, the chief one of which is the source of the excess carbon. Analyses of split ingots have always shown that an average of the carbon determinations has always been several points higher than the ladle tests taken when the ingots were poured. One of the early papers on this subject was that presented by E. F. Kenny,¹⁶ in which he gives the analyses of several split ingots and split blooms rolled from ingots. The ingots and blooms were from a heat showing a ladle analysis of 0.715 C, and the carbon averages of the split ingots and blooms were as shown in Table 6.

The ladle analysis for this ingot is given as 0.51 C, 0.50 Mn; and as in the previous examples, we find the steel at the edge of the ingot to approximate the carbon of the ladle test. The ladle test is of small dimensions and the steel is solidified almost instantly, thereby causing the liberation and reaction of very little of the dissolved gas. (When drillings are taken, this gas appears to be liberated, as we do not obtain the extra carbon in the determination and it has been proved that gases are liberated

¹⁵ J. G. Thompson: Determination of Oxygen, Nitrogen and Hydrogen in Steel. A. I. M. E. *Tech. Pub.* 466 (1932).

¹⁶ E. F. Kenny: Commercial Production of Sound and Homogeneous Steel. Amer. Iron and Steel Inst. (1915).

when steel is drilled.) But with ingots, this freezing of the steel takes place slowly: allowing more gas (CO) to be liberated and it, in turn, reacts with elements of the steel to form their oxides and cause a carbon enrichment at the center of the ingot. We do not say there is no segregation due to selective freezing, but believe our theory gives an explanation for the source of the extra carbon.

TABLE 6.—*Carbon Averages of Split Ingots and Blooms (E. F. Kenny)*

	Carbon, Per Cent		
	Outside	Midway	Center
No. 1 ingot.....	0.717	0.782	0.736
No. 2 ingot.....	0.691	0.766	0.791
No. 3 ingot (rolled into blooms).....	0.719		0.807
No. 4 ingot (average of 19 determinations)...	0.711		0.807

Analyses of the upper half of a split ingot¹⁷ show the following carbon and manganese averages:

Outside	Midway	Center
0.52 C, 0.508 Mn	0.525 C, 0.48 Mn	0.58 C, 0.49 Mn

The writer finds that the results given in the paper by Sims and Lillieqvist appear to confirm his theory on the formation of inclusions. Figs. 11 to 18 show that the steel that was cast in the $\frac{1}{4}$ -in. section (Fig. 11) contains relatively small and few inclusions, and the writer attributes this condition to rapid solidification. As the size of the cast sections is increased, we note an increase in the size and amounts of the foreign matter. Had quantitative determinations been made on cross-sections, we believe the weights of the inclusions would have shown a gradual increase with the increase in the size of the castings. The fact that the two tests cast in the 9-in. sections (Figs. 15 and 16) show the marked uniformity both in size and amount of inclusions gives further indications that the rate of solidification was the controlling factor, as the steel from which the one test was poured was held in the ladle for 22 min. while the other was held for double that time. Had the inclusions been in the liquid steel, there should have been more cleansing action in the second test.

Since the subject of inclusions and their formation has been receiving so much attention during the past few years, various theories have been advanced. The writer has not been able to reconcile the various theories with the amounts of inclusions found in various portions of ingots, and believes his theory fits in with the figures obtained. Since we all know so little about the subject, the writer will appreciate comments and criticisms on his conclusions.

H. SCOTT, East Pittsburgh, Pa.—Perhaps some of the disagreements which have come up between the discussers on inclusions are due to a lack of a clear-cut definition of an inclusion. Apparently, most agree that the silicate inclusions are not soluble in molten steel, and the sulfides are quite soluble in the molten steel, and precipitate out on freezing. Of course, in many cases the inclusions are very complex.

C. E. SIMS and G. A. LILLIEQVIST (written discussion).—In reply to Mr. Kinzel's remark about equilibrium diagrams, we might say that very few quantitative data

¹⁷ Carnegie Steel Co. Handbook on Making, Shaping and Treating of Steel, 466.

were obtained during this study and unfortunately we are not in a position to furnish such diagrams, desirable as they may be. It is hoped that the presentation of this paper will stimulate such work. We seem to differ with Mr. Kinzel on the effect of calcium silicide. His results were obtained on a 0.28 per cent C steel while we obtained ours on a 0.45 C steel. The difference in carbon might easily account for the difference in results. If the carbon is kept sufficiently low, considerable aluminum can often be used without injury to the ductility. In a 0.15 C steel it is difficult to get the inclusions that cause poor ductility.

We are certainly willing to agree with Mr. Larsen that there is some precipitation of inclusions in the liquid steel. This one point, regarding the degree of solubility of nonmetallics, seems to have caused considerable confusion in all the discussion of this paper. In the second paragraph of page 166 we said, "This seems to indicate that the solubility of the nonmetallics is limited and varies with the temperature." Also, in the last paragraph of that page, "Is not this regularity of inclusion content a further evidence of solubility, and does it not attest that the inclusions are present to the saturation point? Any amount over the saturation point seems to be quickly

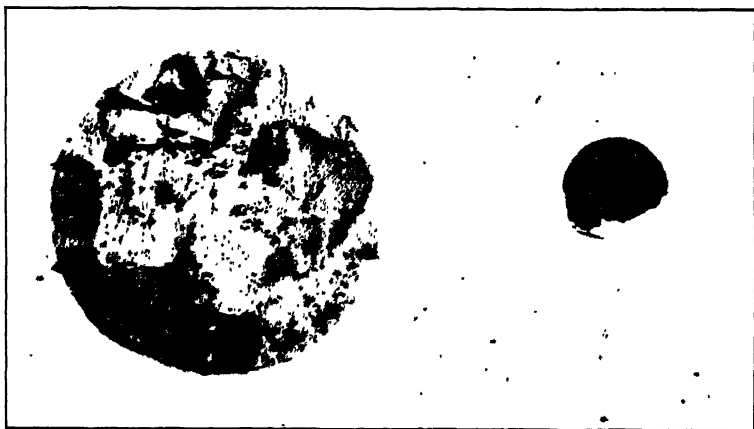


Fig. 26.

Fig. 27.

eliminated from the bath." Our contention is that the solubility is limited and varies with composition and temperature. Although it is limited, it is, nevertheless, large enough to preclude any great hope of obtaining clean steel by the process of levitation, when ordinary methods of deoxidation are used.

Another factor which has led to a difference in opinion has been the failure to distinguish between the natural inclusions and the accidental inclusions. Mr. Larsen found manganese silicate inclusions 1 to 2 mm. in diameter in a rather small test ingot. We, too, have occasionally found such inclusions and their size bears no relation to the section or rate of freezing of the casting. Fig. 26 shows such an inclusion of about 1.2 mm. dia. This, in our opinion, is an accidental inclusion, or, in other words, a particle of slag entrapped during pouring, and it is our belief that the particles mentioned by Mr. Larsen had a similar origin. Such particles are easily distinguished from the natural inclusions by their structure and composition. They have quite a different appearance. Fig. 27 shows the contrast between such an accidental inclusion and the natural inclusions near it.

These slag particles are so very much larger than the largest natural inclusions found even in the center of 15-in. sections that they can hardly be compared. The

largest inclusion found in Fig. 18 was 0.06 mm. dia. The slag inclusion of Fig. 26 is 1.2 mm., or 20 times the diameter of the largest natural inclusion. According to Stokes' law the former should rise 400 times as fast, and if the small inclusions had any appreciable rate of travel it would seem impossible to keep such large ones in the steel as long as a single second.

Mr. Bull's discussion presents a clear picture of the practical aspects of the inclusion problem as it appears to the foundry metallurgist, who is trying to do the best he can with the present available information. We wish to thank him for his commendations.

Mr. Stammer's discussion deserves serious consideration. He discusses at length a probable method of formation for inclusions, which was not touched on in the paper. In No. 5 of the summary, we said, "The normal inclusion-forming material of steel is soluble in the molten state and precipitates as inclusions at the time of solidification." This was intended to infer that the inclusions probably did not exist in simple solution in the same combination as they occur in the solid steel. We do not know how the inclusion-forming material exists in solution but probably it is not as manganese silicate, for instance, or even as SiO_2 . Wahrman¹⁸ touched on this subject in his discussion of solubility.

While Stammer does not agree with our conclusions on many points, fundamentally there is considerable agreement. He believes that at least a fair proportion of the inclusions are formed at the time of solidification from materials previously in solution. This is tantamount to saying that these inclusions are soluble in the liquid steel. He also contends that the actual quantity of inclusions in a piece of steel is largely dependent on the rate of solidification. With this latter view we cannot agree. We know of no empirical data to substantiate this view, while there is considerable contrary evidence. The fact that the content varies in different parts of an ingot is not conclusive evidence because if his theory is correct the center should be the richest in inclusions and not a zone part way in. Stammer suggests that had quantitative determinations been made of the weights of the inclusions they would have shown an increase with the increase in the size of the castings. Since this paper was read some quantitative determinations have been made by Dr. Henry L. Coles, of Hamilton, Ohio, on the 1-in. and 15-in. sections as shown in Figs. 12 and 18, with the following results:

	1-IN. SECTION, PER CENT	15-IN. SECTION, PER CENT
Total slag and oxide.....	0.122	0.102
Fe.....	0.0226	0.0213
FeO.....	0.0291	0.0274
SiO_2	0.036	0.028
Al_2O_3	0.004	0.003

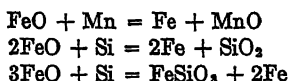
These analyses do not take sulfides into consideration but they do seem to indicate that the smaller section has a slightly greater quantity of inclusions than the larger, in spite of the deceiving appearance to the contrary.

Stammer's explanation of the formation of inclusions is briefly as follows: Carbon monoxide is highly soluble in molten steel, but as the steel cools and solidifies this gas is liberated. If it is liberated slowly enough it reacts with some element in the steel, as for example: $\text{CO} + \text{Mn} = \text{MnO} + \text{C}$. The freed carbon then forms a carbide with the iron and the MnO remains as a constituent of inclusions. Several faults can be found with this theory. In the first place, CO probably does not exist in the steel in simple solution, for it does not obey the laws for solution of a gas in a liquid. The solubility increases with rise in temperature and it is liberated as the steel cools. This is contrary to the behavior of a gas in physical solution in a liquid, and the CO

¹⁸ Reference of footnote 4.

more than likely loses its chemical identity when it dissolves in steel. If it were in solution, why would it have to be liberated as a gas before it could react with such an element as Mn, which is also in solution? However, we do not know, as Stammers says, that from an effervescing or rimming steel quantities of CO are given off as the steel cools and solidifies. It has been demonstrated many times that the FeO-C reaction in steel does not go to theoretical equilibrium and that FeO and C can exist together in steel, if not in equilibrium at least in a state of mutual toleration. An increase in temperature causes an increase in the sum of FeO and C that can exist in steel without reaction. This would explain a widely accepted theory for the liberation of CO from rimming steel. As the steel cools and solidifies the reaction between FeO and C proceeds with the formation of CO and Fe. This seems more reasonable than that CO is held in physical solution.

It is also well known that in the refining of steel if the temperature is kept sufficiently low FeO will oxidize silicon, manganese and carbon in the order given. But if the temperature is raised enough these conditions are reversed and manganese and silicon may be reduced from the slag. This reversal of affinity for oxygen is well illustrated by the bessemer process, where it is possible to retain 1 per cent of silicon while oxidizing the carbon. Therefore, it is apparent that even at moderate temperatures some FeO, Mn and Si can exist simultaneously in molten steel. As the steel cools the quantity of these constituents decreases, and such reactions as



probably take place. In this manner the inclusions are formed at the time of solidification, but the inclusion-forming materials are soluble in the molten steel. Although this explanation is largely hypothetical, it fits the known facts and possibly is the true mechanism of the solubility of inclusions.

We do not agree with Dr. Herty's statement that "coalescence of nonmetallic inclusions has been experimentally demonstrated, and second, that nonmetallic inclusions can be eliminated by allowing steel to stand for a sufficient length of time after deoxidation." If Dr. Herty means by "eliminated" that some portion of the nonmetallics is lost by levitation, there is no argument. In the first place, he does not distinguish between natural and accidental inclusions. The large inclusions mentioned in *Report of Investigations* 3054, page 6, are undoubtedly accidental inclusions. As mentioned in reply to Mr. Larsen's discussion, such large inclusions could not remain suspended in molten steel more than an instant; those nonmetallics in excess of the saturation point are in a condition to float out. But if he means that total elimination can be obtained in this manner, the statement must be questioned. No clean deoxidized steel has yet been produced even experimentally by this or any other method. Wohrman¹⁹ reports on his experiments as follows: "It will be remembered that in most of the experimental melts the inclusion-forming material was allowed to fuse quietly inside of an iron container. No agitation, no stirring was resorted to that could have 'emulsified' the inclusion-forming material, or have caused its uniform distribution throughout the metal. To the contrary, all facilities were provided for the molten inclusion charge to float bodily to the top of the melt if it desired to do so, and yet no such separation took place except in the case of MnS, and even here it occurred to a limited extent only. Instead we found the mechanically included material to be distributed more or less uniformly throughout the metal—to have dispersed, in fact, instead of agglomerated. What mechanism other than dissolution could have accomplished this?"

¹⁹ Reference of footnote 4, 127.

Nor can it be agreed that coalescence of inclusions has been experimentally demonstrated. That inclusions sometimes merge, there can be no doubt, as is evidenced by the club-shaped particle at the top of Fig. 17, of which more will be said later, but coalescence is a hypothecated theory to explain the mechanism of elimination by levitation and the growth of inclusions in large sections.

Cooperative Bulletin No. 36, page 39, says that the two conditions necessary for coalescence are that the particles must be brought into contact and must be fluid at the time of contact. It is suggested that one way in which particles may be brought into contact is that they should be electrically charged, which would give them vibrational mobility. If they were electrically charged they should all have the same charge and would mutually repel each other. However, it is difficult to see how an electrical charge could be maintained in a medium so highly conducting as steel (metallic conductance in this case). Increased concentration should give more chances for collision, and this is given as the reason for the larger inclusions found in the center of an ingot. Although it has been demonstrated that there is some segregation in ingots, the degree of segregation is too slight to account for the very great difference in inclusion size between the outside and center of an ingot or any other casting. Moreover, the maximum concentration seldom coincides with the position of the largest inclusions. (See Figs. 15 and 16 of the bulletin mentioned.) It is illogical to believe that coalescence would take place at an enormously faster rate after the steel has started to freeze, when it is sluggish and pasty, than it would in the ladle where the fluidity and mobility would be much higher. The club-shaped particle in Fig. 17 may indicate that when collision does occur during freezing the sluggishness is too great to be overcome by the surface tension. If it is true, as mentioned in *Bulletin* 36, that the smaller the particle the greater the mobility, then coalescence would tend to be self-limiting.

The second method mentioned for bringing the inclusions together is agitation of the liquid steel, but there is no agitation in the ladle or mold. Therefore, one is left with no means of locomotion for the inclusions except the Brownian movement of colloidal particles. Even with the Brownian movement there would be no collisions except accidental ones.

To quote from *Bulletin* 36, page 41, "The rate of coalescence may be expected to increase somewhat with increasing fluidity." There seems to be no reason to expect the number of collisions to be influenced by the degree of fluidity. Solid inclusions, of course, would not merge even on contact. On the other hand, the clusterlike grouping of alumina or aluminum silicate strongly suggests flocculation of these comparatively insoluble and refractory particles.

Dr. Herty regards as untenable the possibility that oxygen content affects the solubility of the sulfides and gives as his reason that a high silicon addition will deoxidize to the same extent as some lower aluminum addition will. Experience with aluminum indicates that the difference between it and silicon is not merely one of degree. A small addition of aluminum has an effect quite different from a large additional amount of silicon. On the other hand it has been shown that the presence of aluminum is not necessary to obtain the eutectic type of inclusion (Fig. 4).

The effect of aluminum merely represents an extreme condition that serves better the purpose of illustration. Table 4 shows a similar effect in lower degree obtained without the use of aluminum but merely by varying the conditions of oxidation.

It is pleasing to note the correlation between the type of inclusions and physical properties that Mr. Grant reports. The upper two-thirds of his Fig. 24 is typical of a steel having low ductility. The lower third does not represent the same high grade of polishing as the rest and the somewhat blurred spots there are more indicative of polishing stains than inclusions. Mr. Grant does not concur in our observation of the limited variation in the quantity of inclusions to be found in a given class of steel and

as evidence submits Fig. 25. In all of our investigations we have never seen a steel as dirty as this one purports to be. It is our opinion that we could compare notes and find no conflict on this point.

The contribution of Mr. Deschamps gives beautiful confirmation of our observations and conclusions. We had no opportunity to study converter steel but would have been inclined to predict results similar to those reported by him. Converter steel averages better in ductility than electric-furnace steel, for the same reason that open-hearth steel does. The quantity of inclusions is not the controlling factor but rather the degree of oxidation. This points the way toward getting ductile steel from the electric furnace.

Mr. Norris' discussion should be very valuable in clarifying certain points which probably were not emphasized enough in the paper. It is true that what he terms primary inclusions are given but slight consideration but not entirely disregarded. At the bottom of page 166 we said, "Any amount over the saturation point seems to be quickly eliminated from the bath." Our chief concern is not with those that are eliminated but rather with those that remain. The latter may be called secondary inclusions if preferred but no sharp distinction can be made between the primary and secondary types. Our contention is that the secondary inclusions have an importance far overshadowing the primary. In Mr. Norris' classification of secondary inclusions we believe 3 and 4 to be of little moment except possibly in rimming steel.

When the statement was made that "attempts to obtain clean steel by floating out the inclusions were universally disappointing" we meant just that. No clean steel has been made in that manner. It was not meant to infer that there could be no loss in nonmetallics but rather that there would always be enough left to obviate the possibility of clean steel.

We have no quantitative data on the degree of solubility but Mr. Norris' question on this point is at least partly answered in the reply to Mr. Stammler.

Dr. Sosman's discussion of coalescence versus dispersion is extremely interesting and throws some new light on the subject, but it is a matter for discussion by the proponents of the coalescence theory.

Mr. Cantley's remarks are highly appreciated because they indicate that our main objective in writing the paper was at least partly attained. Although we do not believe we have pointed the way to make "clean steel," we hope we have thrown some light on the relation of inclusions to physical properties.

Critical Studies of a Modified Ledebur Method for Determination of Oxygen in Steel

By B. M. LARSEN* AND T. E. BROWER,* KEARNY, N. J.

(New York Meeting, February, 1932)

AN increasing amount of attention is being paid to the possible influence of oxygen, in its several modes of occurrence in steel, upon some of the properties of the metal; but clearly investigations along this line are unlikely to yield significant results until reliable analytical methods for the determination of oxygen have been established. This paper presents some results of a study of an improved Ledebur method which aims to determine a definite portion of the oxygen; namely, that which presumably is present in diffusible form in the solid steel. These more or less preliminary results lead us to believe that the oxygen so determined has some significance; their presentation at this time will, we hope, stimulate discussion of, and focus attention upon, certain rather neglected aspects of the problem. Considerable work has been done recently on methods of estimating inclusions and on the vacuum-fusion method for oxygen; with results which, however, are of somewhat questionable significance.

It is commonly presumed that the oxygen in a bath of molten steel in a furnace is present partly as a separate phase consisting of suspended particles of oxides or silicates, partly in solution, the latter being probably the more important. Upon addition of a deoxidizer, it reacts with some portion of the dissolved oxygen and precipitates it as additional suspended particles; the oxygen not eliminated in this way, which remains in solution in the liquid steel, may be regarded indifferently either as dissolved oxygen or as dissolved FeO. When the steel is poured, some of the suspended particles rise towards the surface, others remain trapped in the finished steel, appearing as nonmetallic inclusions in amounts corresponding usually to about 0.01 to 0.03 per cent O_2 in the steel. The dissolved oxygen may be partly eliminated as CO during freezing of the ingot, but some remains either in solution or in part precipitated as FeO. Finished steels may thus contain oxygen in several forms: (1) In non-metallic inclusions which are probably quite insoluble in the *solid* metal at all temperatures; (2) in solid solution which at lower temperatures may be supersaturated; (3) in FeO particles produced by relief of this

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supersaturation. The oxygen in the nonmetallic inclusions is practically fixed in that form; on the other hand, the oxygen in the other two forms may pass from one to another with changes in temperature, and can diffuse, even if slowly, through the solid steel.

Sources of Error in Oxygen Determinations

The "total-oxygen" or "vacuum-fusion" method, as best described in detail by Diergarten¹ and Jordan,² is intended to determine all three forms by changing all the oxygen present into the dissolved form and pumping it off as CO, CO₂ and H₂O. Since the sample is melted in a graphite crucible, all the oxides containing the so-called "inclusions oxygen" are supposed to be reduced to form either CO or oxygen, in solution in the liquid iron, which can then be extracted by pumping. There are several objections to this method, in addition to the fact that a rather complicated and expensive apparatus is required:

1. It is not at all certain that all the gas contained in a relatively massive portion of liquid metal will diffuse out and be pumped away as completely as is possible when a stream of hydrogen is sweeping over the surfaces of very thin layers of solid metal. For example, Villachon and Chaudron³ melted nickel, iron, copper and aluminum in magnesium oxide crucibles to a pressure of 0.02 mm. Hg at 1700° C. and then treated the same melts after rolling down to 0.1 mm. foil in silica tubes to 0.002 mm. Hg at 1000° C., obtaining appreciable quantities of hydrogen and carbon monoxide in the second treatment. Part of this secondary gas may have come from the silica combustion tubes, but Bircumshaw, in his work on vacuum melting, also noted that the diffusion of gases out of a mass of liquid metal in vacuum was very slow and probably always incomplete. Furthermore, the time of pumping in the vacuum-fusion method cannot profitably be extended very much because after about the first hour the additional amounts of gas obtained are of the same order of magnitude as the blank corrections to the apparatus.

2. It is not yet proved satisfactorily that the Al₂O₃ and other stable oxide particles are completely reduced in this method unless the temperature is raised to a point where blank corrections also increase rapidly. Also the low error caused by the adsorption of gas on films of iron formed by vaporization and condensation is difficult to obviate completely,

¹ H. Diergarten: Determination of Oxygen in Iron and Steel by the Hot-extraction method. *Archiv. Eisenhüttenwesen* (1928-29) 2, 813-28.

² L. Jordan and J. R. Eckman: The Determination of Oxygen and Hydrogen in Metals by Melting in Vacuum. U. S. Bur. Stds. *Sci. Paper* 514 (1925).

H. C. Vacher and L. Jordan: The Determination of Oxygen and Nitrogen in Steels by the Vacuum-fusion Method. U. S. Bur. Stds. *Jnl. of Res.* (1931) 7, 375-401.

³ A. Villachon and G. Chaudron: The Hydrogen and Carbon Monoxide Content of Some Metals Melted in Vacuo. *Rev. de Mét., Mem.* (1930) 27, 368-9; also *Métallurgist* (1930) 6, 144.

especially when these films are high in manganese (*i. e.*, when high-manganese samples are treated).

3. The ratio between "inclusions oxygen" and FeO-oxygen will be rather widely variant in different samples of steel. Also, the accuracy of the known methods of analysis for the oxide inclusions other than FeO is probably at least as uncertain as the total-oxygen method; furthermore, these inclusions are commonly distributed in a very irregular manner. These conditions make it essentially rather hopeless to expect even a roughly accurate determination of "FeO-oxygen" by subtracting the oxygen present as other oxides (determined by residue analysis) from the result of a total-oxygen analysis by vacuum fusion.

All these considerations indicate a possible advantage in the Ledebur method as a direct and more or less specific method of analysis for that portion of the oxygen in steel which can pass into or out of solution and can therefore diffuse in the solid metal. The effects of oxygen in steel probably depend as much on the modes of distribution as on the total amounts present. This FeO-oxygen or "diffusible oxygen" may itself be present (1) in solid solution, (2) as a very finely divided precipitate of FeO particles, (3) as a precipitate of relatively coarse FeO globules and (4) as films of oxide along grain boundaries. Obviously, these various forms might have very different effects on the metal. Therefore if in a certain sample the oxygen present is having an important effect on the metal, a simple determination of the total amount of "diffusible oxygen" present will obviously not tell the whole story. But such an analysis, as compared to a total oxygen determination, should at least eliminate one uncertainty by leaving out nearly all the rather variable amount of oxygen which is present as difficultly reducible oxides, precipitated in the liquid steel; these oxides, which can be present only as relatively large inclusion particles, cannot diffuse into solid solution and assume the other modes of distribution mentioned above. The latest studies have tended to indicate that the effects of inclusions on the properties of steel are in most cases almost too small to be measured, and when they are significant, they tend to be haphazard rather than specific in nature. On the other hand, we do find unexplained and fairly specific differences in quality in certain steels. If any of these effects are caused by oxygen in the steels, we should expect that that part of the total oxygen which is present either in solution or as FeO particles which can most easily pass into solution would be most effective in producing such changes in specific properties. This makes it important to develop a reliable method of directly determining what might be termed the "diffusible oxygen" in steel. These considerations and also the possibility of making a modified Ledebur method more accurate than the vacuum-fusion method, were the considerations leading to the present study of a method using essentially the pure hydrogen treatment of thin layers of the metal in the solid state.

If a method of this sort is to be accurate the elimination of the following sources of error is necessary, according to the experience of previous experimenters:⁴

1. Obviously, the purification of the hydrogen used should be complete enough so that a weighable amount of H_2O , CO or other oxygen-bearing gases will not accumulate from the amount circulated through the train in the course of several hours, and the train itself should be as carefully put together as an ordinary vacuum train.

2. The combustion boat or other vessel containing the sample and any portion of the combustion tube that is heated should not contain even small amounts of iron oxide or other easily reducible oxides, and the material of the containing vessel should not tend to be reduced by hydrogen even when in contact with iron.

3. If the sample is in lump form, the surface area is negligible and the error from surface layers of oxygen inappreciable, but in this case the lumps must be fused up in a metal flux to a melt which will be fluid in the range of 1100° to 1200° C., such as the antimony-tin flux used by Jordan,⁵ Petersen,⁶ and others. A possible extra blank error from the fluxing alloy must be considered in this case. If thin milled layers of sample are used, the oxygen can diffuse out into the surface layers in a reasonable time and no flux is necessary, but the surface area exposed becomes large and the amount of oxygen in this surface becomes of the same order of magnitude as the oxygen actually dissolved in the steel.

4. In the surface layers of a solid iron sample at around 1100° C., atoms of carbon, oxygen and hydrogen are all present and there is a tendency for the oxygen to pass from the solid into the gas phase as molecules of either CO or H_2O . The ratio between these two gases will not be definite but probably will vary with the speed of hydrogen

⁴ J. R. Cain: Determining Gases in Steel and the Deoxidation of Steel. *Trans. A. I. M. E.* (1918-19) **62**, 185-210.

J. R. Cain and L. Adler: Equilibrium Conditions in the System Carbon-iron Oxide, and Hydrogen in Relation to the Ledebur Method for Determining Oxygen in Steel. U. S. Bur. Stds. *Sci. Paper* (1919-20) **15**, 353-66.

P. Oberhoffer, E. Piwowarsky, E. A. Pfeifer-Schiesl and H. Stein: Gas and Oxygen Determinations in Iron, Especially Pig Iron. *Stahl u. Eisen* (1924) **44**, 113-16.

B. Kjerman and L. Jordan: A Study of the Hydrogen-antimony-tin Method for the Determination of Oxygen in Cast Irons. U. S. Bur. Stds. *Jnl. of Research* (1928) **1**, 701-20.

H. Petersen: A Contribution to the Problem of Oxygen Determination in Iron by the Hydrogen-reduction Method. *Archiv. Eisenhüttenwesen* (1930) **3**, 459-72.

J. R. Cain and E. Pettijohn: A Critical Study of the Ledebur Method for the Determination of Oxygen in Iron and Steel. U. S. Bur. Stds. *Tech. Paper* **118** (1918).

^{5,6} Reference of footnote 4.

circulation, the temperature and the amount of carbon in the sample. This means that to recover all the oxygen, the amounts of both gases (plus a small amount of CO_2) must be determined in the gases issuing from the combustion tube.

EXPERIMENTAL METHOD

The best supply of hydrogen would be electrolytic hydrogen produced as needed right in the laboratory. A good grade of electrolytic hydrogen can now be obtained in tanks, however, and was used in the present work. Tank hydrogen made from water gas may also be obtained, but always contains small amounts of carbon monoxide, which is very difficult to remove completely from the gas. The electrolytic hydrogen contains as impurities only small amounts of carbon dioxide, oxygen, water and nitrogen. The purification train used was designed to combine a large capacity with a very nearly oxygen-free product. Fig. 1 represents a general outline diagram of the train arrangement finally used. The hydrogen tank is connected by heavy rubber tubing to a sulfuric acid bubbler tube 1, passing next to a U-tube 2 filled with an 8 to 10-mesh granular drying agent such as calcium chloride or "Dehydrite." Next is a soda-lime tower 3 of rather large capacity for the removal of carbon dioxide, and the hydrogen then passes over a mass of platinized asbestos about 10 in. long, packed in a silica tube *C* and heated to 800° to 850° C. in an ordinary split-type nichrome-wound tube furnace 4. This fused silica tube is connected to the glass system by vacuum-wax joints *A* and *B* and is made extra long so that these wax connections do not need to be water-cooled. This long length of platinized asbestos at 800° C. can be depended upon to convert all the oxygen in the gas to water vapor and it was either very insensitive to poisoning at this temperature, or else no catalyst poisons were present in the tank hydrogen used. The hydrogen then passes through a large calcium chloride tower 5, a one-way stopcock 6, a small P_2O_5 drying tube 7 and another one-way stopcock 8. Stopcock 6 is inserted here simply to make it possible to shut off the preceding portion of the train and remove and refill tube 7 without cooling down furnace 4. As long as a small portion of the full cross-section of tube 7 is filled with dry P_2O_5 , one may be certain that the hydrogen purification is complete.

The heating furnace (18) for the sample tube is a small Globar resistance furnace designed for maximum temperatures of 1300° to 1400° C. It was controlled with a Pt-Pt-rhodium thermocouple and a recording potentiometer regulator, with a circuit arranged to give a temperature regulated to $\pm 2^\circ$ to 3° C. In the first train set up for this work the furnace tube *E* and the heating furnace 18 were placed horizontally, but for reasons given in a later section this was changed to the vertical arrangement indicated in Fig. 1. The furnace tube *E* for heating

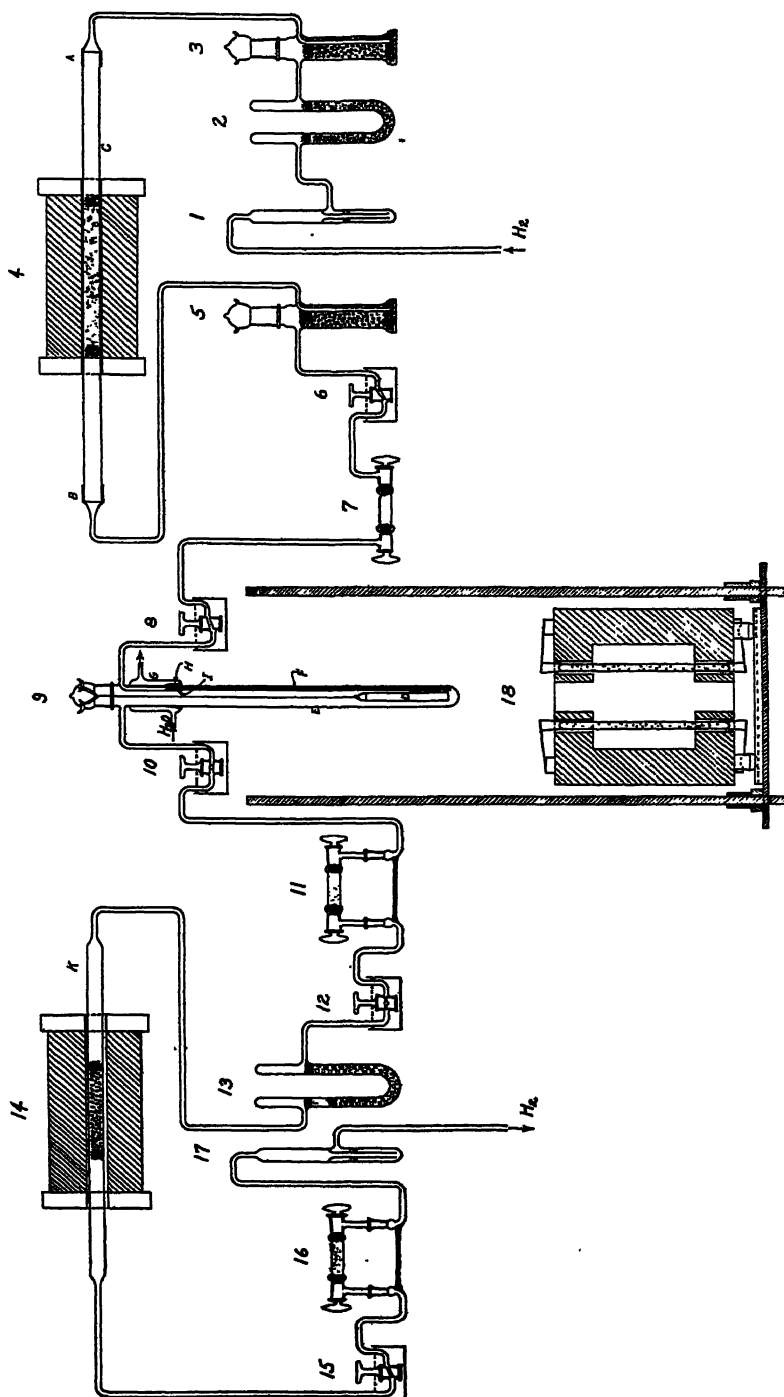


FIG. 1.—TRAIN FOR DETERMINATION OF OXYGEN IN STEEL.

the sample is 18 in. long by $1\frac{1}{8}$ in. inside diameter and is of transparent fused quartz, which has at least three important advantages for the present purpose: (1) It contains no easily reducible oxide impurities such as FeO , which would give a troublesome blank error; (2) the position of the sample can be seen; (3) the furnace 18 heated to the full operating temperature (usually around 1100° to 1130° C.) can be rapidly moved around or away from the tube *E* so that very little time is lost in heating and cooling the sample.

The open end of the silica tube is connected to the water-jacketed glass fixture 9 with vacuum wax at point *H*. This water-cooling was found to be necessary to keep the wax from softening (chiefly caused by heat radiated along from the hot portion in the tube walls and absorbed by the opaque wax). *D* is a cylinder of thin iron foil closed at the bottom, large enough to hold 30 to 35 g. of thin steel millings, and suspended out of contact with either the silica heating tube or the thin transparent silica delivery tube *F*, which is sealed with wax at *I* to the hydrogen inlet tube. The outgoing gases pass to T-cock 10, where they may either be wasted out the side tube of the T-cock, or be passed on to No. 1 weighing tube 11, which is filled with anhydrous P_2O_5 or "Anhydron" (anhydrous magnesium perchlorate), and which removes all the oxygen present as H_2O coming from the sample. Next is T-cock 12, where the gas stream may again be either flushed out the side tube or passed on to U-tube 13, filled with copper sulfate on pumice stone (dried at 150° to 160° C. for 3 to 4 hr.) as recommended by Fresenius⁷ to remove all H_2S from the gases before they enter the catalyst furnace 14 to prevent poisoning of the catalyst surfaces. It has been found necessary to use a double U-tube here. Most of the H_2S is absorbed at the entrance to the first tube, but the last traces are deposited at scattered points on through both tubes. At the exit end of the second tube a small amount of anhydrous P_2O_5 is placed to insure that no traces of water vapor from the tubes enter the rest of the train. Furnace tube *K* is of glass containing the reduced nickel-thoria catalyst, which converts the CO and CO_2 in the gases to H_2O and CH_4 and the water vapor formed is absorbed in No. 2 weighing tube 16 after passing through the one-way stopcock 15. The hydrogen stream passes out to the air through sulfuric acid bubbler tube 17.

This train is in most essentials similar to that used by Petersen.⁸ Pyrex glass is used throughout, with either glass to glass or vacuum tight wax seals, and with all ground joint connections made to be as nearly vacuum tight as possible. The stopcocks are all clamped in small welded sheet-iron troughs, and completely immersed in mercury, after the method

⁷ R. Fresenius: *Zitsch. anal. Chem.* (1871) 10, 75.

⁸ Reference of footnote 4.

developed by Shepherd⁹ in his work on the analysis of gases extracted from rocks. Except possibly for this mercury immersion of the stopcocks, the other precautions to insure a tight train are very important for accurate analysis with this method.

MECHANISM OF DEOXIDATION OF THIN LAYERS OF STEEL

The available data on the gas-metal systems from a number of sources form a fairly convincing mass of evidence for the conclusion that in nearly all cases a gas is dissociated into atomic units when dissolved in a metal, and that in diffusion of gases through metals, the gas diffuses as atomic units in solid solution in the metal. The whole subject is too extensive to discuss here in detail, but if we assume the above condition to be substantially true, we may picture the deoxidation of steel by hydrogen or by vacuum extraction as follows: If hydrogen is circulated over layers of solid steel it is adsorbed on their surfaces, where the H_2 molecules are partly dissociated into H atoms, and these immediately begin to diffuse into the metal, tending ultimately to saturate it with hydrogen. At the same time, there will be a tendency for oxygen atoms on the surface and perhaps in the first molecular layers of iron to combine with the adsorbed hydrogen and evaporate as H_2O molecules. If carbon atoms are present on this surface they also will tend to evaporate as molecules of CH_4 , CO and CO_2 . If the temperature is high enough to give an appreciable speed of diffusion of oxygen, as well as of hydrogen and carbon, the dissolved atoms of carbon and oxygen will begin to diffuse out to the oxygen-free surface layers and evaporate as additional CO and H_2O molecules. In this way, the metal will be gradually deoxidized and at a rate dependent only upon the rate of diffusion of oxygen atoms in the solid iron lattice, since there will always be an excess of either carbon, hydrogen or both at the surface to combine with the oxygen atoms as fast as they reach this surface by diffusion. This mechanism supposes that units of H_2O , CO or CO_2 do not form inside the iron lattice, or if they occasionally exist temporarily as such units in the iron, they cannot diffuse as such in the metal.

If the metal layers are simply heated in vacuum, exactly the same process will occur, but here the only source of hydrogen to form H_2O molecules will be the small amount of hydrogen usually present in solution in steel, and proportionately more of the oxygen will evaporate as CO molecules. Also, the metal will be completely deoxidized by vacuum heating only if there is an excess of carbon above that amount equivalent to the oxygen present in the metal, because the dissociation pressure of FeO is extremely low, even at 1100° to 1200° C.; too low to be reached by a vacuum pump.

⁹ E. S. Shepherd: *The Analysis of Gases Obtained from Volcanoes and from Rocks. Jnl. Geol.* (1925) **33**, Sup. 3, Apr.-May.

Available data indicate in a qualitative way that hydrogen will diffuse in iron at an appreciable rate at temperatures down to 100° C. or lower. At temperatures of about 550° C., or even lower, carbon diffuses through an appreciable distance in a few hours, but the rate for oxygen is very much smaller, and in a limited time diffusion of oxygen does not become appreciable below about 950° to 1000° C. The reaction between hydrogen and iron oxide becomes appreciable at temperatures of around 200° C. or even lower. These facts indicate that in the range of about 200° to 500° or 550° C., hydrogen should react with surface layers of adsorbed oxygen or iron oxide to form H₂O, but very little CO or CH₄ should be formed. In the 600° to 900° range, both H₂O and CO should be formed if surface oxygen is present on the sample, and an appreciable amount of CH₄ should be formed, but relatively little elimination of the oxygen in solution in the layers of iron should occur. Above 1000° C., CH₄, CO and H₂O should all be formed, both from oxygen on the surface and from oxygen and carbon dissolved in the steel.

COMPARISON OF HYDROGEN REDUCTION WITH VACUUM EXTRACTION OF OXYGEN FROM STEEL AT AROUND 1000° TO 1200° C.

Either thin layers of solid iron or lump samples melted in tin-antimony alloy may be analyzed for gases by simply heating the sample in vacuum at 1100° to 1200° C. and collecting the gases evolved by any standard method, such as that used by Oberhoffer¹⁰ and by Klinger.¹¹ According to the experience of Villachon and Chaudron,¹² such a method should give about as high a percentage recovery as in the other methods, of the gases and oxygen present as easily reducible oxides, as long as there is present an amount of carbon more than equivalent to the oxygen present. This becomes one limitation of the method as compared to the Ledebur method, since in a limited number of samples such as ingot iron, electrolytic iron and certain vacuum-melted alloys all the oxygen could not be extracted by this method. The method has the advantage that nitrogen, hydrogen and oxygen are all determined at once. It also has the advantage over the Ledebur method that the oxygen-bearing gases are not diluted with very large volumes of hydrogen, which make the determination of CO much more difficult. On the other hand, the gas-collecting pump and analysis apparatus, vacuum pumps and gages make the system rather complicated.

Certain sources of blank error in the Ledebur method, such as the reduction of oxide impurities in refractories by hydrogen, would not be

¹⁰ P. Oberhoffer and A. Beutell: The Determination of Gases in Iron. *Stahl u. Eisen* (1919) 39, 1584-90.

¹¹ P. Klinger: The Determination of Gases in Iron and Steel. *Stahl u. Eisen* 1926) 46, 1245-54, 1284-8, 1353-8.

¹² Reference of footnote 3.

present with vacuum extraction. On the other hand, one apparently very important error in this method is the difficulty of eliminating the continuous evolution of gases from refractory walls when heated in vacuum. Heindlhofer, in a preliminary study made in this laboratory of gas evolution from steel, found that the rate of evolution of gases from surfaces of fused quartz and porcelain heated in the 1000° to 1300° C. range decreased only very slowly with time, even when the tubes were pumped for a period at 1300° C. and then cooled to 1100° C. again. The indications were that a period of several days of pumping at 1300° to 1400° C. would be necessary to reduce the blank error from this source to a low value. This source of error may be removed by suspending the sample from a wire in an evacuated Pyrex bulb and heating only the sample itself by a high-frequency induction coil, after previously baking out the glass surfaces in vacuum. From the experience of Cioffi at the Bell Telephone Laboratories, however, one apparently escapes here from one difficulty only to encounter another. At 1100° C. or higher, the rate of evaporation of iron is fairly rapid, so that an iron film is soon formed on the cold glass walls near the sample, and this cold metal film seems to absorb (or adsorb?) an appreciable fraction of the gases given out by the sample.

If thin millings are used for the samples in the vacuum extraction method, one again encounters the error from surface oxide on the very large exposed surfaces of such metal chips. With samples containing an excess of carbon, the possibility of removing this surface oxide by a preliminary lower temperature heating was indicated by one of the experiments made by Heindlhofer. A sample of thin steel strip (about 0.003 in. thick) containing about 0.8 per cent C., was first pumped almost free of gases at about 1100° C. and cooled in vacuum. This was then removed, heated just long enough on a hot plate to form a blue oxide film on the surfaces, and replaced in the vacuum set-up, the train evacuated, closed off and the furnace heated up gradually. Between about 500° and 600° C. the pressure began to increase markedly but the reaction did not become very rapid until a temperature in the range 600° to 650° C. was attained. After about 5 to 6 hr. heating at 640° to 660° C. the reaction was apparently nearly complete, and the rate of gassing dropped to a comparatively low value until the temperature was again raised to values approaching 750° C. This would indicate that at around 600° to 670° C., carbon began to diffuse out fairly rapidly from inside the iron to combine with the oxide surface layers, forming CO and CO₂, with probably very little removal of the oxygen inside the sample. The process is rather slow, however, but as indicated in discussion below, if hydrogen is passed over the metal surfaces, this removal of surface oxygen seems to occur at much lower temperatures and to be completed in a much shorter time, probably in large measure due to the fact that in a hydrogen stream the reaction is

not limited by the slow diffusion of carbon to the surface from inside the metal lattice.

DETERMINATION OF OXYGEN EVOLVED AS CO OR CO₂ IN THE LEDEBUR METHOD

Any oxygen evolved as H₂O from the steel sample in the Ledebur method is relatively easy to determine with sufficient accuracy by simply passing the gases through a weighing tube containing any one of a number of efficient water absorbents such as P₂O₅ or anhydrous magnesium perchlorate. If even small amounts of carbon are present in the steel, however, an appreciable percentage of the oxygen is given off as CO and CO₂. The relative amount of CO₂ is probably nearly negligible in such a case, because in a gas phase which is nearly pure hydrogen the equilibrium mixture of these several gases under these conditions is such that practically no CO₂ would remain.

The accurate determination of very small amounts of CO in the presence of an excess of hydrogen is a relatively difficult analytical problem. Several methods might be developed for the purpose, but it is very desirable to choose the most simple method. After consideration of possible physical methods, it was decided that they would not be specific enough and it would be difficult to maintain a check upon their accuracy. Of various possible chemical methods, one might consider (1) the reaction of CO with hot iodine pentoxide solutions, (2) the selective oxidation of CO to CO₂ in the presence of a catalyst, and (3) the conversion of CO to methane and water in the presence of a catalyst as discovered by Sabatier.¹³

The reaction with iodine pentoxide was first used¹⁴ in this country about 1918, and the method was modified and improved by Jordan and Kjerman¹⁵ at the Bureau of Standards. In this method the gas is passed through iodine pentoxide heated to about 150° C., then through potassium iodide solution to remove the iodine liberated, dried with CaCl₂ or H₂SO₄ and P₂O₅ and the CO₂ formed then absorbed in an ascarite weighing tube. Free iodine present tends to react with stopcock grease in near-by points. Also, hydrocarbons which are always present in small amounts may also be partly oxidized to carbon dioxide by the iodine pentoxide.

The selective oxidation of CO to CO₂ over catalysts has not been studied very much and there might be some doubt as to the possibility of making it quantitative with small amounts of CO in large volumes of hydrogen. It was then noted that Petersen¹⁶ had recently made a study

¹³ P. Sabatier and B. Senderens: A New Synthesis of Methane. *Compt. rend.* (1902) **134**, 514-6.

¹⁴ J. R. Cain: Reference of footnote 4.

^{15,16} Reference of footnote 4.

of the use of the methane catalysis reaction as applied to the Ledebur method and obtained very good results, and this procedure was therefore followed in the present work. The reactions between hydrogen and carbon monoxide and carbon dioxide,



are both catalyzed by freshly reduced metallic nickel, which was first discovered by Sabatier and Senderens¹⁷ about 1902, and this process has been given very extensive study since that time, so that the most favorable conditions of temperature, composition of catalyst, etc. are now definitely established. The most important advance since the original discovery by Sabatier has been the use of so-called "promoters," which usually are oxides of other less easily reducible metals, which when intimately mixed with nickel oxide in amounts of from 3 to 20 per cent will give the mixture, after reduction with hydrogen at temperatures below 400° C., a much greater catalytic activity than the straight Ni + NiO catalyst. Medsforth¹⁸ gives the results of a comparative study of various promoters on the activity of the reduced nickel catalyst. He finds that ceria, thoria, chromium oxide, alumina, silica and zirconia decrease in activity as promoters in the order named, the relative activity of ceria compared with thoria being in the ratio of 103.6 to 100. With thoria-nickel mixtures the most favorable proportions were around 10 per cent of thoria to 90 per cent of nickel. The temperature of initial NiO reduction should be below 400° C. and the most favorable operating temperature for the catalyst around 270° C. Petersen¹⁹ found that, with a similar thoria-nickel catalyst on a base of porcelain chips, operating at around 250° C., both CO₂ and CO gases were quantitatively converted to water and methane when present in an excess of hydrogen. Petersen also removed H₂S (to prevent poisoning of the catalyst) from the gases passing to the catalyst by the method of Fresenius in which 60 g. of porous pumice stone is soaked with a solution containing around 30 to 35 g. of copper sulfate, the water boiled away and the pumice heated in a drying oven around 3 to 4 hr. at 150° to 160° C.

In the present apparatus, the catalyst was made up in the usual standard way, by soaking about 30 g. of acid-washed porcelain chips in a strong solution containing 15 g. Ni(NO₃)₂·6H₂O and 0.65 g. Th(NO₃)₄·4H₂O, boiling off the water, and igniting the mass gently around 350° C. to drive off all nitric oxide gases. This heating should not be prolonged

¹⁷ Reference of footnote 13.

¹⁸ S. Medsforth: Promotion of Catalytic Reactions. *Jnl. Chem. Soc.* (1923) 123, 1452-69.

¹⁹ Reference of footnote 4.

beyond the time necessary to drive out these gases. The mass was placed between glass wool plugs in a 20-mm. Pyrex glass tube. This tube was then sealed in series with the double U-tube filled with copper sulfate on pumice stone. The catalyst furnace was simply hand regulated, which, in spite of ordinary line-voltage variations, was good enough to hold the furnace within the 250° to 270° C. temperature range, which gives most rapid reaction rates.

With the mode of connection of the catalyst tube described above and shown in Fig. 1, the catalyst and the copper sulfate could be kept always in an atmosphere of pure, dry hydrogen, since all entrained air in the line could be flushed out through the side tube of T-cock 12 and there were no openings into the catalyst tube except through the two mercury-covered stopcocks. This is important, because, no matter whether the catalyst furnace is cooled to room temperature or is kept hot between determinations, the enormous exposed surface of reduced nickel will react rapidly with any oxygen present.

After setting up the train, the catalyst furnace was heated to 325° to 350° C. and dry hydrogen passed through for about 60 hr. After cooling the catalyst to 260°, the train gave a blank value over 3 hr. of 0.1 mg. in No. 1 tube and 2.8 mg. in No. 2 tube, showing incomplete reduction of the catalyst. The weighing tubes were replaced and the catalyst again heated to around 350° to 360° C. and the blank at this temperature determined for successive periods. In the next 16 hr. the blank was 22 mg., and 1.6 mg. in 1 hr., and after about 44 additional hours the blank was about 0.7 to 0.8 mg. per hour. After 48 additional hours the blank was about 0.6 mg. per hour and when the catalyst furnace was cooled to 260° C., the blank was about 0.1 to 0.2 mg. per hour, which was considered fairly satisfactory. It apparently required about 5 to 6 days of continuous reduction at 350° to 360° C. to reduce the nickel oxide sufficiently so that at 260° C. the blank value becomes negligible. During this period the blanks on the No. 1 tube averaged about 0.1 mg., varying from -0.1 to +0.3, indicating that the train as a whole was in a satisfactory condition. With further operation of the train these blanks tended to decrease very slowly.

Petersen²⁰ determined the efficiency of this catalyst by circulating measured volumes of pure CO and CO₂ mixed with a large excess of hydrogen. This method is rather cumbersome to use in routine checking of the train, so in the present case, a small amount of pure calcium carbonate crystals was accurately weighed into a combustion boat, placed in the combustion tube, and heated slowly up to 950° to 1000° C. and then held there about one hour, with the hydrogen circulating constantly through the train at the same rate as in the analysis of a steel

²⁰ Reference of footnote 4.

sample. Under these conditions, CO_2 should be slowly liberated from the carbonate and in the gas phase should react with hydrogen to form somewhere near the water-gas equilibrium mixture with a great excess of hydrogen; i. e., about equal amounts of CO and H_2O and a much smaller residual amount of CO_2 . The gain in weight in the first tube is, of course, the amount of H_2O formed, and the gain in weight of the second tube should be the weight of water equivalent to the oxygen in the CO and CO_2 . Table 1 gives the results of a few determinations made in this way. The blank corrections are just a little arbitrary, being about the average of blank determinations made about the same time.

TABLE 1.—*Efficiency of Catalyst as Measured by Analysis of Oxygen as CO_2 in pure CaCO_3*

Weight of CaCO_3 , grams.....	0.1000	0.1002	0.1297
H_2O in No. 1 tube, mg.....	16.1	12.8	19.8
H_2O in No. 2 tube, mg.....	21.7	22.6	26.9
Total weight H_2O , mg.....	37.8	35.4	46.7
Blank correction, mg.....	1.0	0.4	0.4
Net weight H_2O , mg.....	36.8	35.0	46.3
Theoretical H_2O , mg.....	36.0	36.0	46.7

At a later period when the catalyst had been maintained at 230° to 260° C. steadily for several weeks, without running any checks on carbonate in the meantime, a suspiciously high value for the oxygen in a steel sample was obtained. The checks with pure carbonate were run immediately in which values of 47.4 and 46.0 mg. were obtained, the theoretical value being only 44.0 mg. in both cases. Strangely enough, the blank value on the train at this time was only 0.2 mg. in each weighing tube, indicating that perhaps the catalyst would lose a little oxygen only when the hydrogen contained some CO and CO_2 . The catalyst was then heated again to 350° C. and yielded 6.3 mg. water in about 15 hr. After 4 hr. more at 350° C., the catalyst was cooled again to 260° C. and three checks with carbonate run during the next 10 days (during which time, the catalyst was reduced three separate times overnight at 350° to 75° C.) gave the following values:

Weight CaCO_3 , Grams	Actual Weight H_2O , Mg.	Theoretical Weight H_2O , Mg.
0.1131	40.9	40.7
0.1137	41.0	41.0
0.0760	26.8	27.3

This error from the catalyst may have been caused by an accidental inlet of oxygen to the nickel through an open stopcock, or it may have been caused by a gradual readjustment in the catalyst layer, exposing

new nickel oxide molecules to the gas phase, which would then reduce on heating to 350° C. after long standing at 260° C. Later the catalyst was treated many times in flowing hydrogen at 325° to 350° C. and, although the weight of water vapor formed by the reduction in 14 to 16 hr. decreased slightly, the reduction of the NiO to completion would apparently require an extremely long time at this temperature. It is possible that most catalyst bodies made up in this way are never pure reduced nickel but are always mixtures of reduced nickel plus small residual amounts of NiO. In fact, it is possible that a reduced nickel catalyst is always a Ni-NiO catalyst with the catalytic effect largely resident in the boundary points between metal and oxide phases, and that the addition of a "promoter" merely substitutes another more active oxide for the NiO.

However this may be, the evidence above seems to prove that such a catalyst body, if given a preliminary reduction of about a week at 325° to 350° C. and subsequently given an occasional further reduction at this temperature in overnight periods, will quantitatively convert such small amounts of CO and CO₂ to H₂O and CH₄ without contributing any appreciable blank error of its own at an operating temperature of 250° to 270° C. No evidence of any poisoning of the first catalyst used was noted until after about six months' operation. The check with pure CaCO₃ should be made occasionally, however.

ELIMINATION OF ERROR DUE TO SURFACE OXYGEN ON SAMPLES OF THIN MILLINGS

The use of thin millings has several advantages: (1) It is possible to obtain a more nearly average sample of any portion of large bars or ingots; (2) the maximum distance that the oxygen in solution must diffuse is small and nearly definite; (3) the area of contact between sample and container is much smaller than with a melted charge in a boat or crucible; (4) the oxygen value obtained should nearly correspond to the portion of the oxygen that can diffuse in the solid lattice; that is, to the portion of the oxygen that is in solid solution, or which can pass into or out of solid solution.

Against these possible advantages, the one definite disadvantage lies in the error caused by the large surface area exposed to oxidation by the air either during or after cutting of the millings. With millings cut around 0.003 to 0.004 in. thick, this error has been found to correspond to around 0.02 to 0.04 per cent O₂ for samples milled slowly in air with the piece at room temperature during cutting. The area of such chips is indeterminate, but such an amount of oxygen must correspond to many molecule layers of oxide. Cain and Pettijohn²¹ endeavored to avoid this error by cutting their samples under oil, washing with benzene,

²¹ Reference of footnote 4.

drying in dry air and storing in desiccators previous to the analysis. This technique reduced the blank error to about 0.003 to 0.005 per cent O_2 . They found this residual error to be very nearly constant and practically proved that it was due to oxidation of the surfaces by short exposure to air at room temperature.

This small error might be larger with samples handled at a location where the atmosphere is more corrosive. Also, the operations of milling under oil, washing, etc., are very tedious and time consuming. In the present work, the attempt was made to separate the surface oxygen from that actually contained in the space lattice of the sample, by a preliminary reduction at a much lower temperature than that required for the final determination of the true oxygen content. A bessemer steel analyzing C 0.092 per cent, Mn 0.32, P 0.086, S 0.049, N_2 0.012, O_2 0.043, (oxygen determined by the present method as described in a later section) was cut into 0.004 in. thick millings at a slow rate in air, with no special precautions, except that no contamination of the sample by oil or scale was permitted. A 10-gram sample of this steel was first treated with hydrogen for 90 min. at 1050° to 1070° C. in the combustion tube and the weights of water obtained were 3.7 mg. in tube 1 and 4.2 mg. in tube 2. Allowing the blank correction, this corresponded to about 0.061 per cent O_2 . Later 30.88 g. of this same sample of millings was treated in a large boat, but heated in stages to various temperatures as indicated below in Table 2.

TABLE 2.—*Oxygen Obtained from a Sample of 30.88 Grams of Millings of a Bessemer Soft Steel Treated for 1 Hr. at Various Temperatures*

Temperature of Sample, Deg. C.	Weight H_2O in Tube 1, Mg.	Weight H_2O in Tube 2, Mg.	Total H_2O , Mg.	Total Minus Arbitrary Blank Averaging About 0.2 Mg.	Total Cumulative H_2O , Mg.
200-220	3.6	0.1	3.7	3.5	3.5
400-420	5.3	0.0	5.3	5.1	8.6
500-515	2.2	0.2	2.4	2.2	10.8
595-615	0.5	0.1	0.6	0.4	11.2
695-705	0.2	0.2	0.4	0.2	11.4
800-805	0.3	0.5	0.8	0.6	12.0
880-885	0.7	0.5	1.2	1.0	13.0
920-930	0.3	0.7	1.0	0.8	13.8
1000-1015	1.3	0.8	2.1	1.9	15.7
1090-1105	2.3	2.5	4.8	4.6	20.3

The weight of water from this sample corresponding to the figure of 0.061 per cent obtained in one heating stage at 1050° to 1100° C. would be 21.3 mg., which is a rough check on the value of 20.3 mg. cumulative weight obtained by the various steps in Table 2. No better check would be expected, considering the uncertainty of the cumulative blank correction. The most logical interpretation of these results is to assume that

even at a temperature of as low as 200° C., the hydrogen was beginning to react with the surface oxygen on the millings. The rate was very slow, and even after another hour at 400° C., the removal of surface oxygen was incomplete. After another hour at 500° C., the surface layers were apparently almost stripped of their oxygen content, since in another hour at 600° C. only 0.4 mg. more H₂O was obtained. At 700°, the weight obtained is still lower (0.2 mg.) but begins to increase slightly at 800° (0.6 mg.) and 880° C. (1.0 mg.), which we may assume is the beginning of an appreciable diffusion outward of the dissolved oxygen in the first few outside layers of the iron lattice. The temperatures of 880° and 925° were employed in succession to determine whether any marked increase in diffusion rate would result from the conversion of the metal from mostly alpha to all gamma iron. The weights of water obtained (1.0 and 0.8 mg., respectively) indicate no marked change. As the temperature approaches 1000° C., the rate of diffusion begins to increase much more rapidly (1.9 mg. H₂O in 1 hr.), and between 1000° and 1100° there is a still larger increase, to a value of 4.6 mg. H₂O in 1 hr. at 1100° C.

It is also significant (Table 2) that up to 600° C. practically none of the oxygen was removed as CO and CO₂, while at the maximum temperature about one-half the oxygen evolved was in this form. This simply means that below 600° C., the rate of carbon diffusion to the surface layer was extremely slow compared to the rate of reaction of hydrogen with the oxygen at the surface, and is in line with the assumption that compound gases are formed and evolved at the surface after the constituent atoms have separately diffused to this surface either from the gas phase or from the solid solution phase. In this experiment mentioned above in which thin foil was heated in vacuum, the surface oxygen evolved fairly rapidly only at around 650° C. or above, but even at these temperatures the rate was much lower than in hydrogen at 500° C., because in the vacuum experiment the carbon had to diffuse out from solid solution before any CO molecules could be formed at the surface. These results in general support the belief that at 500° C. very little of the dissolved oxygen will be lost, since we know with fair certainty that oxygen diffuses in iron solution more slowly than carbon, and since the results indicate that even carbon diffuses only very slowly at 500° C.

Another sample of the same steel (20 g. millings) was heated for successive periods at around 500° C. and the cumulative H₂O obtained is shown by the curve in Fig. 2. This curve flattens out fairly sharply after a period of around 40 to 60 min. These results on the whole indicate that at a temperature of around 500° C. the rate of removal of "surface oxygen" is perhaps 90 to 95 per cent complete in a period of around 60 to 70 min. On the other hand, the fact that the outward diffusion of oxygen inside the space lattice begins to be rapid only when the temperature is around 500° C. higher than the temperature range at

which hydrogen reacts rapidly with the surface oxygen affords a reliable basis for the assumption that the separation of surface and dissolved oxygen can be made quantitative to an accuracy of around ± 5 per cent. Probably, in samples very high in oxygen containing many FeO inclusions, this separation would be less accurate; probably a slightly larger amount of the true oxygen content of the sample would be lost at 500°C . from the many exposed surfaces of FeO particles at the surface of the millings. However, for ordinary steels, at least, the accuracy indicated was considered good enough to warrant using the method of low-temperature hydrogen treatment to remove surface layers of oxide.

The method finally adopted was to insert the sample of millings in a boat or in a thin iron foil cylinder (with the vertical furnace tube arrangement in Fig. 1) into the cold combustion tube with all stopcocks closed, then close the cap on the combustion tube head, increase the pressure in

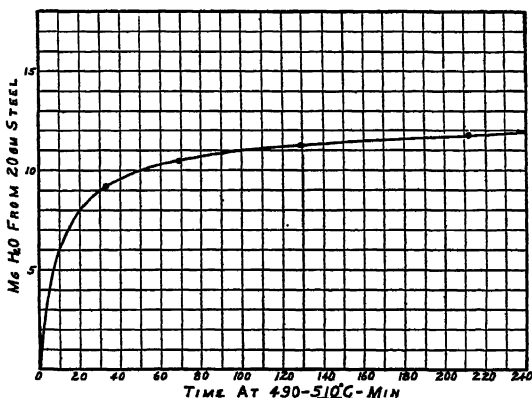


FIG. 2.—RATE OF EVOLUTION OF SURFACE OXYGEN AS WATER VAPOR FROM 20 G. OF 0.003-IN. MILLINGS AT 490° TO 510°C .

the hydrogen purifying train, open stopcock 8 leading from the hydrogen supply to the combustion tube, and then set T-cock 10 so that the hydrogen passed out the side outlet. The tube and boat were flushed free of air in this manner for 10 to 12 min. and an auxiliary heating furnace, previously adjusted to a temperature of about 500° to 550°C . was then moved to surround about 10 in. adjacent to the closed end of the transparent silica combustion tube. After this reached about 500°C . the hydrogen circulation was continued for a period of 60 to 75 min., wasting all the gas out of T-cock 10. This cock was then turned to connect with the rest of the train, the auxiliary furnace lowered and moved away, the inlet and outlet connections to No. 1 weighing tube (11) opened and T-cock 12 turned to waste hydrogen through the side outlet. After 4 to 5 min. the train up to the catalyst furnace was free of air and T-cock 12 was connected to the catalyst tube, the remaining stopcocks

opened and hydrogen bubbled through the whole train 2 to 3 min. longer. The whole train was now considered filled with pure hydrogen, and the sample was practically free of oxygen on its surfaces but still contained essentially all of the original oxygen present in the massive sample before it was cut into chips.

Cock 8 was now turned to shut off the supply of hydrogen and the main Globar heating furnace at 1100° C. was raised up around the furnace tube. With the furnace up to temperature and regulated to about $\pm 3^\circ$ C., the hydrogen supply was turned on and bubbled steadily for usually from 120 to 180 min. The Globar furnace was then lowered away from the combustion tube. After about 10 min. more, all stop-cocks in the train were closed, the weighing tubes removed, their greased surfaces thoroughly cleaned with ether, hung in a box with the counter-poise tube, and allowed to stand near the balance about 5 min. before weighing. During this period the cooled sample could be removed from the tube, another weighed sample inserted, and the train flushed out and heated to 500° to 550° C. to remove surface oxygen, while the tubes were being weighed after the previous determination.

The amounts of "surface oxygen" obtained at 500° to 550° C. as outlined above have varied from 0.031 to 0.048 per cent in samples of millings analyzed to date. In a few comparative cases there was a tendency for higher oxygen samples to give a higher apparent surface oxygen, but in all such cases the millings from the higher oxygen samples contained noticeably greater amounts of fines, which would increase the surface and at least partly account for the higher values for surface oxygen. In one instance, two samples, one of which contained 0.042 to 0.044 per cent and the other 0.019 to 0.020 per cent oxygen by analysis, gave approximately the same degree of fineness in their millings. These samples both gave values for surface oxygen within the range of 0.031 to 0.033 per cent, which of course is what should result if the separation of surface oxygen from dissolved oxygen is nearly quantitative, since the amount of oxide formed on the surface of millings made and handled according to a definite procedure should be independent of the oxygen content of the sample.

BLANK CORRECTIONS WITH VARIOUS COMBUSTION BOATS

In the first set-up, a horizontal furnace tube was used and it was necessary to determine the amount of blank error from combustion boats and from steel millings in contact with such boats. These are really somewhat different conditions. Absolutely pure iron or absolutely dry oxygen-free hydrogen has a zero oxygen pressure. We approach these conditions as closely as possible, and believe that any refractory oxide will be reduced very slowly by either the sample or the hydrogen. Such reactions appear to be slow enough to neglect in such an analysis in the

case of all oxides except FeO , but there is the further possibility that the reaction with certain other oxides will be catalyzed where the oxide is in contact with reduced metal at 1100°C .

The first blanks obtained with just the empty transparent silica tube heated to 1050° to 1100°C . averaged around 0.1 mg. per hour, which is quite satisfactory. Transparent silica boats heated in this tube gave, of course, the same low blanks, but it was noticed that when a sample of steel millings was heated in such a boat, additional water kept on coming off even after many hours at 1100°C ., and the cumulative oxygen value became suspiciously high. One of these boats was lined with thin platinum foil and in 1 hr. at 1100° to 1110°C . gave a blank value of 3.5 mg. Upon removal the platinum foil was found to be stuck very tightly in spots to the inner surface of the boat, and parts of the foil were very brittle and crumbly, presumably due to the absorption of reduced silicon. This, of course, is analogous to the contamination of platinum thermocouples when in contact with silica in the presence of reducing gases, and iron apparently will cause the same effect at a slower rate. Steel millings 0.003 to 0.004 in. thick, even after heating for 20 to 30 hr. or more at 1100°C ., gave blank values of never less than about 1.0 to 1.5 mg. per hour at this temperature in silica boats. A boat of sillimanite porcelain gave somewhat lower blanks of around 0.6 to 0.8 mg. per hour with this same highly reduced sample of millings, and about 0.3 to 0.4 mg. per hour when empty.

A number of other porcelain, alundum and zirconia bodies were then tried, but they all gave blank values of from 0.6 to 5 or 6 mg. per hour even when empty and still larger blanks when filled with highly reduced millings. In these cases the bodies all darkened to gray or black upon hydrogen treatment, indicating that iron oxide (or other easily reducible oxides) was present, perhaps as an impurity in a clay bonding material. The following materials all showed this effect to a greater or lesser extent:

Porcelain. D-4 Masse, Staatliche Porzellan Manufaktur, Berlin.

Porcelain. Sillimanite, Champion Spark Plug Co.

Alundum. Norton Co.

Alumina. "Aloska," Steatit Magnesias Aktien Gesellschaft.

Zirconia. Deutsche Gold-und-Silber Scheideanstalt.

A few boats of C.P. grade magnesium oxide were then made up in the laboratory, using essentially the method described by Mehl.²² This involved shrinking the light fluffy MgO first in a large graphite steel-melting crucible to about 1100°C ., then heating to around 1800° to 1900°C . in a pure graphite crucible in the induction furnace to eliminate practically all the remaining shrinkage and grinding in an agate mortar to about 100 mesh. This material is then mixed to a thin paste with an

²² R. F. Mehl, J. L. Whitten and D. P. Smith: Laboratory Production of Pure Magnesia Ware. *Ind. & Eng. Chem.* (1925) **17**, 1171-2.

absolute alcohol-shellac mixture, packed in a boat-shaped graphite mold with a collapsible wooden core, the core removed, the mass dried several hours or overnight at room temperature, heated very slowly to 150° to 160° C. in a drying oven, held 2 hr. and then heated in the graphite mold, with a graphite cover (plus large graphite blocks above and below) in the induction furnace, packed in finely divided carbon insulation, to about 1800° to 1900° C. for about 30 to 40 min., and cooled in the furnace.

These boats resisted sudden temperature changes very well and gave practically zero blanks when heated empty in hydrogen at 1100° C. One of them was then filled with the same highly reduced sample of steel millings and the surface oxygen again removed at 500° as usual. At

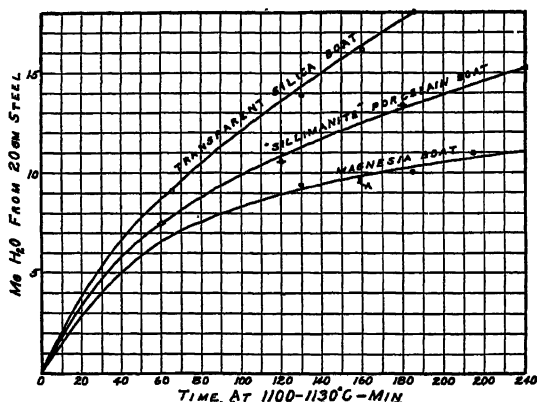


FIG. 3.—OXYGEN EVOLUTION FROM THE SAME STEEL AT 1100° C. BUT WITH DIFFERENT BOAT CONTAINERS, SHOWING VARIATIONS DUE TO SIDE REACTIONS OF HYDROGEN WITH THE REFRACTORIES IN THE PRESENCE OF IRON.

1100° C. for 1 hr. this combination gave a total blank of only 0.3 mg., which was much lower than for any of the other boats. Such boats, made to a size of about 90 to 100 mm. long, 20 mm. wide, and 14 to 15 mm. deep, were used in many subsequent determinations. Fig. 3 shows the cumulative weights of water obtained from successive periods of heating at 1100° to 1130° C. with three different 20-gram samples of bessemer steel, all taken from the same bottle of millings, but placed in boats of transparent silica, sillimanite porcelain and magnesia, respectively. In each case the surface oxygen on the sample was first removed by heating for 1 hr. at 500° to 550° C., and the sample left in the closed furnace tube between successive periods of heating. In blank runs with almost completely deoxidized millings, the transparent silica boats gave the highest blanks (1.0 to 1.8 mg. per hour), and the special magnesia boats the least (0.3 mg. per hour). The curves in Fig. 3 are qualitatively in agreement with these values and show clearly the large cumulative error caused by very slow side reactions.

With the magnesia boats there is still a residual upward slope to the curve even after 4 hr. heating. As some later tests have rather conclu-

sively shown, the first portion of the curves of oxygen evolution follows closely the form of a theoretical diffusion curve for heat energy or any dissolved substance out of a solid of the form of an infinite slab; that is, where the diffusion is almost entirely perpendicular to one plane in the sample. This means that the oxygen evolved up to the point where the curve of evolution straightens out to a constant upward slope (approximately point *A* in Fig. 3) is what might be called "diffusible oxygen"; that is, oxygen present either in solution or in some form such as FeO particles, which can pass quickly into solution and thus move according to the simple diffusion law. If this was the only source of oxygen present, the curves should gradually flatten out to a zero slope, and the more or less constant evolution beyond this first 2 to 3-hr. period indicates

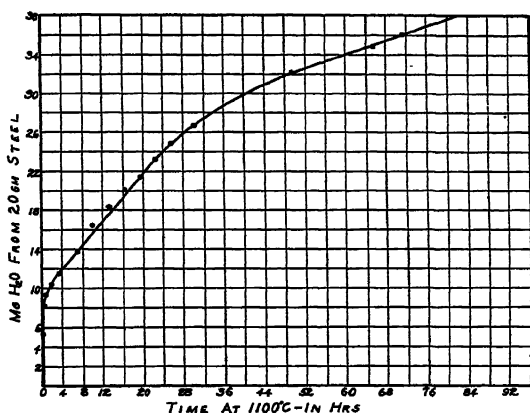


FIG. 4.—A LONG-TIME EVOLUTION CURVE OF OXYGEN FROM A SAMPLE OF 0.0016-IN. STEEL FOIL AT 1100° C.

a secondary source from which the rate of evolution is limited primarily by some other process than diffusion. This source might be (1) a slow reduction of the silica tube or of the material in the boat, or (2) a slow reduction of the oxide and silicate inclusions in the steel sample. To eliminate the boat as a possible source of this secondary oxygen, the whole train was rebuilt at this time and arranged with a vertical furnace and tube as in Fig. 1, so that the sample could be suspended in the hydrogen out of contact with any hot refractory oxide surface. A container of thin steel foil (0.0015 in. thick) perforated with tiny holes and formed into a $\frac{1}{2}$ -in. dia. cylinder closed at the bottom, was suspended by a platinum wire in the furnace tube. Its weight was about 2 g. This was then heated alone in the furnace at 1100° to 1120° C. for about 18 hr., after which the rate of oxygen evolution had dropped to about 0.2 mg. of H₂O per hour. Twenty grams of low-carbon, high-oxygen 0.0016-in. steel foil was then placed in this container, heated at 500° to 550° C. as usual for about an hour to remove surface oxygen and then heated for

successive periods at 1100° to 1105° C., giving the curve of oxygen evolution shown in Fig. 4. (The time scale is much condensed in this graph as compared with Fig. 3.) After about the first 100 min. of heating, the curve of evolution straightens out to a constant slope, which has about the same value as the curve beyond point A for the magnesia boat in Fig. 3. This indicates that the pure magnesia boats were not contributing any appreciable blank error. The amount of water formed up to this break in the curve corresponds to about 0.044 per cent of "diffusible oxygen" in this particular steel.

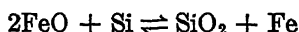
If the oxygen evolved after this first period comes entirely from some side reaction and not from the sample, it should continue to be formed indefinitely at about the same rate, but if all or part of it comes from the sample, the rate should decrease after sufficient time. To test this, the heating was continued for a total of about 175 hr., only about 96 hr. being shown in Fig. 4. After about 20 hr. the rate of evolution began to fall off gradually from the first rate of about 0.6 mg. per hour and after about 48 hr. had dropped to a value of about 0.15 mg. per hour, which remained practically constant up to the end of the 175 hr. of heating. Immediately after this long run, the sample was removed quickly from the furnace tube, and the latter closed up and heated again to the same temperature (1100° to 1105° C.) with hydrogen circulating as usual to determine the blank on the train without the sample, and this was found to be -0.04 to -0.05 mg. per hour (total weight change in both weighing tubes, of course). The cause of this small but definite negative value probably is due to the use of anhydrous P_2O_5 in the hydrogen purification train, while "Anhydron" (anhydrous magnesium perchlorate) was used in the weighing tubes. Apparently the train as a whole happened to have practically a zero blank at this time, while the perchlorate tended to lose a little water to the hydrogen dried over P_2O_5 . Adding this value of -0.05 mg. per hour to the $+0.15$ mg. per hour with the sample present (after 96 to 175 hr. heating) gives a blank correction of 0.2 mg. per hour. We have not been able to determine the cause of this small blank (practically all of which is evolved as H_2O and recovered in No. 1 weighing tube). We have usually subtracted a blank of about this value in making the determinations of "diffusible" oxygen, although the correction is too small to make any important change in the values for oxygen content.

If the last portion of the curve in Fig. 4 is extended back to the zero axis we obtain an intercept which corresponds to about 0.095 per cent O_2 . This we might interpret as being a "total oxygen content," and since the "diffusible oxygen" is apparently around 0.044 per cent this would indicate that about 0.05 per cent O_2 is present combined as oxide or silicate inclusions, which would give a not unreasonable value for inclusions content. It is perhaps worth noticing that during the early part of this run most of the oxygen was recovered in the No. 2 weighing tube from CO

evolved by the sample and that this CO-oxygen dropped gradually to zero by the end of the first 48 hr. of heating. Such a method is a very poor way of determining "total oxygen," not only because of the impossibly long time required, but because of the fact that the blank correction (which is always slightly variable) becomes very large over such a long period; however, it seems probable that some of the extra oxygen recovered after the "diffusible oxygen" is removed comes from the inclusions in the steel. Since it has been shown that a fused silica boat is reduced by hydrogen at 1100° C. when in contact with iron, it is reasonable to expect that silicate inclusions would be reduced slowly by iron, which is very low in dissolved oxygen and contains dissolved carbon and hydrogen.

SOME MISCELLANEOUS ANALYSES FOR DIFFUSIBLE OXYGEN

Table 3 gives a few analyses for diffusible oxygen in various samples by the method described above. The values vary from about 0.013 per cent O₂ in a tool steel containing 0.22 per cent Si to 0.042 per cent in a bessemer soft steel with practically no silicon in solution. In a rough way, the oxygen contents decrease consistently with increasing silicon contents. In the two tool steels and the two spring steels given, the residual silicon probably determines the diffusible oxygen content, since no oxygen was lost as CO gas during freezing and since silicon was the "strongest" deoxidizer used in making these heats. The values for oxygen vary in an inverse way with the silicon contents, but all the values for oxygen are several times larger than those given by Herty and Fitterer²³ in their study of the equilibrium in the reaction



existing in the deoxidation of steel with ferrosilicon. In their work, the oxygen determinations were made by the simple Ledebur method, with no provision for recovering CO and CO₂ from the gases evolved, which probably accounts for most of the discrepancy in this case. It has been assumed generally that in very low-carbon steels this error due to oxygen evolution as CO rather than H₂O could be neglected, but we have found in the present work that even in ingot iron containing around 0.02 per cent C or less, about 25 per cent of the oxygen is evolved as CO. In soft steels containing around 0.10 per cent C about 60 to 70 per cent of the oxygen is recovered from CO in No. 2 weighing tube and 30 to 40 per cent as H₂O in No. 1 tube, and with steels containing around 0.80 per cent C, the gain in weight on No. 1 tube just about corresponds to the blank on the furnace and train, so that practically 100 per cent of the oxygen is evolved from the sample of thin millings in the form of CO (plus probably a very small amount of CO₂).

²³ C. H. Herty, Jr. and G. R. Fitterer: Deoxidation with Silicon and the Formation of Ferrous-silicate Inclusions in Steel. Carnegie Inst. Tech. Metallurgical Investigations, *Bull.* 36 (1928).

The analyses for ingot iron in Table 3 are rather interesting in that they show the difference in ingot segregation of oxygen and nitrogen. The nitrogen contents are practically the same in the "core" and "rim" zones of the ingot, while oxygen is nearly twice as high in the ingot core. This probably indicates that the solubility of FeO is much less in the solid than in the liquid iron at its melting point, while the corresponding change in nitrogen solubility is relatively very small.

Table 3 gives some check analyses for total oxygen by the vacuum-fusion method, which were made at the Bureau of Standards through the courtesy of Mr. J. G. Thompson and Mr. H. C. Vacher according to the method as described by Vacher and Jordan.²⁴ The nitrogen analyses given were run at this laboratory by the ordinary solution-distillation method and also at the Bureau of Standards by the vacuum-fusion method. The nitrogen contents obtained by both methods are in satisfactory agreement.

TABLE 3.—*Miscellaneous Analyses on Commercial Steels*

Sample	Carbon, Per Cent	Silicon, Per Cent	Man- ganese, Per Cent	"Diffusible" Oxygen by Modified Ledebur Method, Per Cent	"Total" Oxygen by Vacuum- fusion Method, Per Cent	Nitrogen by Solution Distillation Method, Per Cent	Nitrogen by Vacuum- fusion Method, Per Cent
Electric furnace tool steel.....	1.00	0.22	0.28	0.011	0.005	0.010	0.010
Electric furnace tool steel.....	1.06	0.16	0.20	0.016	0.004	0.012	0.016
Bessemer rimmed steel	0.05	0.008	0.34	0.032	0.027	0.011	0.011
Bessemer soft steel.....	0.09	trace	0.32	0.042	0.034	0.012	0.011
Basic open-hearth soft steel.....	0.09	0.029	0.39	0.024	0.025	0.006	0.004
Basic open-hearth spring steel.....	0.76	0.21	0.72	0.011		0.0046	
Basic open-hearth spring steel.....	0.82	0.18	0.73	0.015		0.0044	
Ingot iron, core of ingot				0.076		0.0077	
Ingot iron, rim of ingot				0.043		0.0071	

There is, however, a definite tendency for the "total oxygen" values by the vacuum-fusion method to run lower than the corresponding "diffusible oxygen" values obtained by the modified Ledebur method as presented here. These differences would not be quite so serious if both methods were presumably giving the same fraction of the total or the total oxygen present in the steels, but when what is apparently only a part of the oxygen present obtained by one method gives larger values than the corresponding values assumed to be "total oxygen" values obtained by the other method, there is obviously something wrong with one or both methods of analysis; at least as they are applied to the analysis of commercial steels.

²⁴ Reference of footnote 2.

In an analysis of this sort, it is practically impossible to prepare a really satisfactory standard sample, and any judgment of the accuracy of a method must be based chiefly on the consistency of results and the elimination of uncorrected blank errors. We have not yet been able to find any source of error that would cause the present method to give appreciably high results. The elimination of surface oxygen seems to complete itself rapidly at 500° to 550° C., and one would more likely suspect that this removal would tend to make the final results a bit low because of the removal of the dissolved oxygen in the extreme surface layers of iron than that the results would be made appreciably too high. With magnesia boats or previously deoxidized steel foil, the true blank correction for the train and for side reactions (which is not more than about 0.2 to 0.4 mg. per hour) is so low that possible variations in its value would not affect the results to any significant extent. In later analyses new foil containers often have been used and the blank correction determined as follows: A new foil cylinder (these are made of 0.0015 by 2 $\frac{3}{8}$ -in. steel ribbon and weigh about 2 g.) is heated to 500° to 550° C. to remove surface oxygen and then heated at say 1115° to 1120° C. for 150 min., the total oxygen evolution from train and container being determined. For each sample a new foil container of nearly the same weight of the same steel as before is used, filled with 25 to 30 g. of the sample of thin millings and the whole heated at the same temperatures for the same time, the weight from container alone being subtracted from the weight from container plus sample. One more or less standard sample which had been run in a magnesia boat several times, giving 0.041 per cent, 0.042 per cent, and 0.044 per cent O₂ was run in this manner and gave 0.042 per cent O₂. The conditions in the determination of this blank are exactly reproduced in running the sample except that a greater weight of steel is present in the furnace tube.

In the first part of this paper several possible causes for low or irregular results in the vacuum-fusion method have been suggested. It is possible that the reduction of inclusions and the extraction of the gases in solution in the mass of liquid iron does not approach completion as rapidly as has been assumed in the studies made on the vacuum-fusion method. The whole question cannot be decided arbitrarily at present and points to the necessity for further careful tests of both methods of analysis.

In some recent experiments on the rates of deoxidation of the same steel when rolled into thin ribbon of various thicknesses, the results have indicated that the rate of extraction of the "diffusible oxygen" follows closely the simple form of Fourier's linear diffusion law. The results at present are very incomplete, but we may perhaps record briefly the essential result of the preliminary experiments. Fourier's law for linear diffusion may be most simply expressed in its differential form as

$$\frac{dc}{dt} = k \frac{d^2c}{dx^2}$$

where c would be the concentration of oxygen at any plane parallel to and at distance x from the surface of the ribbon at time t , and k is a diffusivity constant. The integration yields complicated equations which show that at a given temperature the time required for a given fractional elimination of the oxygen present should vary inversely as the *square* of the thickness of the metal. The preliminary results obtained to date with samples of foil differing only in thickness agree closely with this relation, and the curve obtained fits the theoretical curve based on a constant value for the diffusivity of oxygen in steel at the temperature 1100° C. These experiments, it is expected, will be described in a later paper.

SUMMARY

The results of this preliminary study of an improved Ledebur method have been encouraging, with indications that what is termed here the "diffusible oxygen" can be determined within 5 to 10 per cent of the amount present in this form. A method of this kind may have some practical importance, since it seems likely that this so-called diffusible oxygen is more likely to exert a significant influence upon the properties of steels than that contained in the almost insoluble, indiffusible inclusions.

The reduced nickel-thorium oxide catalyst apparently gives a quantitative conversion of carbon monoxide and carbon dioxide to water vapor and methane and is not very susceptible to poisoning or other causes of deterioration. These results are a check upon the conclusions of Petersen,²⁵ who first applied this catalytic reaction to the Ledebur method. The determination of oxygen in CO₂ from pure calcium carbonate crystals is apparently an accurate and simple method for checking the efficiency of the catalyst and of the train as a whole.

It is apparently possible to remove the surface oxygen on thin millings or any thin layers of iron by heating for about an hour at 500° to 550° C. without removing appreciable amounts of the dissolved or FeO-oxygen in the iron. It is not yet possible to measure the absolute accuracy of this separation, but the results indicate an accuracy of ± 5 per cent or better. Occluded or adsorbed oxygen in the furnace tube or sample is also completely removed by this low-temperature reduction, and the method is easier to use and at least equal in accuracy to the preparation of millings under oil proposed by Cain and Pettijohn.²⁶

The fraction of the oxygen determined that was evolved as CO or CO₂ instead of H₂O in this method varied from as little as 15 to 25

^{25,26} Reference of footnote 4.

per cent in ingot iron up to practically 100 per cent in higher carbon steels, such as spring steel with 0.75 to 0.9 per cent C.

The existence of a slow reaction between silica and pure hydrogen at 1100° at points of contact between the silica and either iron or platinum is fairly definitely established. This, together with the apparent presence of reducible oxides (probably iron oxide) in various commercial porcelain, alundum or zirconia boats, caused appreciable errors which were eliminated only by the use either of pure magnesia boats or of a vertical furnace tube with the sample suspended in a cylindrical container of thin steel foil. Even with these arrangements, there was apparently a blank of about 0.2 mg. H_2O per hour, the source of which could not be ascertained definitely. With a carefully constructed train and a transparent quartz tube heated to 1100° to 1130° C., *but with no steel sample present*, the blank values obtained were less than 0.1 mg.

The pure magnesia boats prepared in the laboratory from C.P. MgO invariably induced a rapid recrystallization of the transparent silica furnace tubes. This is thought to be due to the presence of traces of alkalis in the magnesia, and might not be encountered if boats of either pure magnesium oxide or pure beryllium oxide low in alkalis could be prepared. With the vertical furnace tube arrangement, the fused quartz tubes gave a satisfactory life at 1100° to 1130° C.

From samples of commercial steel foil of constant thickness ranging from 0.0016 to 0.0066 in., the rate of evolution of oxygen followed closely the simple diffusion law until a large fraction of the diffusible oxygen had been removed. After this period there was a slow evolution of additional oxygen, which is thought to be partially derived from a slow reduction of oxide and silicate inclusions in the steel.

Comparative analyses indicate that the vacuum-fusion method for total oxygen in commercial steels may give low results, for in pairs of several identical samples the so-called "total oxygen" was definitely lower than the "diffusible oxygen" determined by this modified Ledebur method.

ACKNOWLEDGMENTS

The authors are much indebted to Dr. John Johnston for direct supervision and advice throughout the progress of this work; to Dr. K. Heindlhofer for suggestions derived from his preliminary experiments on the vacuum extraction of gases from steel; to Mr. E. E. Legge of the American Steel & Wire Co. for helpful cooperation in securing special steel samples; to Messrs. H. C. Vacher and J. G. Thompson of the Bureau of Standards, who have been most courteous and helpful in making comparative oxygen and nitrogen analyses by the vacuum fusion method; and to Miss Elizabeth Keedick for nitrogen analyses by the solution-distillation method.

DISCUSSION

(E. C. Bain presiding)

F. G. NORRIS, Middletown, Ohio (written discussion).—As the authors have well pointed out, oxygen may be present in steel in several forms. Also there are several methods for the determination of oxygen, among which may be mentioned vacuum fusion, hydrogen reduction and residue methods. It is not surprising that none of these methods is without its particular limitation, and that each must be used and the results interpreted with regard to these limitations. Rather fortunately quite complete information can be secured by the combined use of the available methods.

We feel that use of carbon crucibles and of pressures under 0.02 mm. will minimize the possibility that the vacuum fusion method does not remove all of the oxygen from the melt. Low increase in weight after successive 30-min. applications of the vacuum indicate that practically all of the CO that will be removed is removed in the first 30-min. period.

The hydrogen reduction method as developed by the authors should prove of value in the determination of the soluble or "diffusible" oxygen. We wish to congratulate the authors on reporting their results in terms of oxygen without committing themselves as to the possible molecular identity of this oxygen, since it is probable that the oxygen came from oxides both of iron and of manganese.

We suggest that a sample of ingot iron is the best kind of material to use to compare the results of the hydrogen reduction method with the vacuum-fusion method. There is no silica which may be determined by vacuum fusion and not by the hydrogen reduction and there is insufficient manganese to cause low results. Referring to Table 3, it is regrettable that vacuum-fusion oxygen is not reported for the ingot-iron samples.

The rate of purification of iron by hydrogen has recently been extensively studied at the Naval Research Laboratories and I am indebted to Dr. R. F. Mehl for some of the data which I believe are pertinent to this discussion. Strips of selected Armco ingot iron $\frac{1}{16}$ -in. thick were analyzed for oxygen by the vacuum-fusion method before and after treatment with hydrogen (Table 4).

TABLE 4.—*Purification of Iron by Hydrogen*

Temp. of Purification, Deg. C.	Percentage of Oxygen (by Vacuum Fusion)							Condition of Hydrogen
	Initial	After 48 Hr.	After 92 Hr.	After 94 Hr.	After 140 Hr.	After 142 Hr.	After 264 Hr.	
1000	0.030	0.011		0.004		0.005		Dried
1200	0.030	0.002			0.002			Undried
1200	0.030		0.010		0.006			Dried
1220	0.030						0.007	Dried

We conclude that under the experimental conditions some oxides cannot be reduced by hydrogen, and some oxides which can be reduced by hydrogen are not reduced in 48 hr. Reduction may be faster using undried hydrogen than when using dried hydrogen.

J. H. SCAFF, New York, N. Y.—In discussing the vacuum-fusion method for determining oxygen, the authors say that it is not at all certain that all the gas in the molten sample will diffuse out and be pumped away. From the meager data available

on this subject, it seems to me that the rate of evolution of the gas from the sample would be faster than the rate of reduction of the more refractory oxides such as alumina and that substantially all the gas produced by the reduction of oxides would be evolved during the time used in the analysis. It is true that the last traces of gas are difficult to remove by vacuum treatment, but I believe that the quantity of this residual gas is small when compared with the total quantity of gas produced by the reduction of oxides.

There is another point which I believe will be of interest to anyone engaged in oxygen determinations, whether they are using the vacuum-fusion or the Ledebur method. In either of these methods, it is necessary to weigh a very small quantity of water or carbon dioxide—usually about four milligrams. To do this the water vapor or carbon dioxide is usually absorbed in P_2O_5 or ascarite in a weighing tube whose weight is of the order of 75 grams. In order to weigh 4 mg. in a container weighing 75 g. it is necessary to use weighing methods accurate to six significant figures.

At the Bell Telephone Laboratories, some work is being done on oxygen determinations in which the quartz spring method is used to weigh the small quantity of CO_2 and H_2O . The gas is absorbed in a suitable absorbent which is contained in a small basket suspended from the quartz spring. The springs can be constructed with any sensitivity desired, so that it is possible to weigh small quantities of H_2O and CO_2 with high accuracy. With the springs now in use for oxygen determinations, the absorption of $\frac{1}{2}$ mg. of CO_2 or H_2O by the absorbent extends the spring 1 mm. The extension is measured by a cathetometer and from previous calibration it is possible to convert the reading of the spring extension to the weight of the material absorbed. I believe the quartz spring method can be used to great advantage in oxygen determinations.

A. SAUVEUR, Cambridge, Mass.—It seems to me that the question of combined oxygen versus total oxygen is one of great importance, and that if we are going to be able to find out only how much total oxygen we have in the steel without having any idea of how much is included as oxygen inclusions and how much is in solid solution, we are not going to go very far. I would like to ask Mr. Larsen whether in his opinion his modified Ledebur method enables him to obtain the total oxygen, or whether he is getting dissolved oxygen, or something between the two.

E. C. BAIN, New York, N. Y.—Professor Sauveur calls attention to a very important consideration in this whole matter. We have been in the habit of going through certain analytical formulas and getting numbers. Certainly part of the proper function of this symposium is to try to find out, if possible, just what it is that we determine in the various methods, and to define the thing accurately, if possible.

J. G. THOMPSON, Washington, D. C.—At the Bureau of Standards we have been interested primarily in the vacuum-fusion method, and to date have believed that the vacuum-fusion method recovers completely the oxygen from easily reducible oxides. We have considerable data on hand to substantiate that belief. For that reason we have been particularly interested in trying to account for the higher results that Messrs. Larsen and Brower got on given samples than we could obtain with the vacuum-fusion method. One possibility occurred to us, and I would like to ask the authors whether they have considered it. That is the possibility of the formation of ammonia from the nitrogen present in these steels, and the subsequent inclusion of that ammonia as water in the first weighing or two.

Mr. Vacher tried one or two preliminary experiments the other day and proved to our satisfaction that ammonia is evolved from the steel. In his experiment he obtained something like five or six thousandths of a per cent of ammonia. That

would not completely account for the discrepancy in the results, but would be in the direction of helping to account for them.

Another point is in the blank correction which is necessary in this Ledebur method, the arbitrary sharp distinction between the surface oxygen and what you might call the body oxygen, the oxygen which is dissolved and is really a part of the metal. There is still a little doubt in my mind as to just how sharp that dividing line may be. It seems, perhaps, possible that the evolution of the last traces of the surface oxygen and of the first traces of the dissolved oxygen, which is present immediately under the skin of the metal, would overlap, and that perhaps a shift in the blank determination could be made to lower the apparent results slightly.

B. M. LARSEN (written discussion).—Mr. Scaff raises the question of accuracy in the weighing of the amounts of 2 to 20 mg. of water vapor obtained in this method. The quartz springs used at the Bell Laboratories have certain advantages such as greater speed and, under certain conditions, greater accuracy than the chemical balance. The latter is an old institution, but should not be frowned upon for that reason if in any particular application it will give sufficient accuracy, which seemed to be the case in our experiments. A good balance should be accurate to 0.1 mg. when loaded to not more than around 150 g. on each pan. The bulbs we used weigh about 70 g. but could be made much lighter if necessary. The balance will distinguish a variation in them of 0.05 mg., and it is possible to remove a bulb, clean and weigh it, replace it in the train, remove, clean and weigh again, and check within the accuracy of the balance in most cases, the ordinary variation being about ± 0.1 mg. The balance has certain advantages again over the use of quartz spring suspensions, such as (1) greater simplicity, with no need for special calibration or for very skilled technique in making and using the absorption bulbs, and (2) the use of large amounts of absorbent through which all the gas must circulate.

The question of how much residual gas is left in a mass of liquid metal after vacuum treatment is an open question, which must wait upon the accumulation of more data.

Dr. Sauveur's pertinent question as to what oxides are reduced in the Ledebur method is difficult to answer. Iron oxide is of course quantitatively reduced, and dissolved oxygen is also recovered; SiO_2 and MnO are not reduced at appreciable rates at 1100°C . in the absence of iron, but recent data from several sources indicate that in the presence of iron MnO begins to reduce appreciably at around 950° to 1000°C . and SiO_2 at around 1050° to 1100° , so that the Ledebur method probably recovers at least some of the oxygen from these oxides and from silicates. There are indications, however, that the rate of oxygen recovery from oxygen combined with or dissolved in the iron is more rapid than from these other oxides and it may be possible to distinguish between these quantities on this basis.

Dr. Mehl's data on the rate of reduction of $\frac{1}{16}$ -in. layers of Armco iron show that the rate of reduction by hydrogen is very slow at 1000° , which is in agreement with the low values for oxygen diffusivity obtained in the present work. Three samples of Armco iron which we have analyzed have all been within the range of 0.045 to 0.08 per cent oxygen, compared to the value of 0.03 per cent in Mehl's sample. The residual amounts of oxygen not reduced by the hydrogen in Mehl's sample may be largely from aluminum oxide, which is probably not reduced in the Ledebur method, but the long reduction period found necessary is probably due only to the thick samples used, since the diffusivity constant is very small and the time for a given fractional deoxidation varies with the square of the thickness.

The indications of ammonia formation obtained by Mr. Thompson and Mr. Vacher are very interesting and rather surprising, since the amounts of ammonia formed are much larger than would be expected from the data on the equilibria between ammonia, hydrogen and nitrogen, which indicate that ammonia should be

almost completely dissociated into hydrogen and nitrogen at 1000° to 1200° C. The extent of interference from this source must remain an open question until further tests have been made.

Since this paper was written, further long-continued runs on samples with higher carbon have indicated that the relative blank error is much larger with higher carbon contents in the steel. This means that with high-carbon and low-oxygen steels the method as given is still not adequate for precise results. Further work is being carried out, using high-frequency heating, so that no very hot silica surfaces are exposed to the possible reducing action of hydrogen containing traces of iron vapors and hydrocarbon gases.

The Equilibrium Diagram of Iron-manganese-carbon Alloys of Commercial Purity

BY E. C. BAIN,* E. S. DAVENPORT* and W. S. N. WARING,* KEARNY, N. J.

(New York Meeting, February, 1932)

THE more familiar compositions of both the iron-carbon-chromium¹ and the iron-carbon-tungsten² systems have been investigated with a degree of thoroughness which has permitted the construction of their three-dimensional equilibrium diagrams; and it is probable that these equilibrium diagrams are sufficiently accurate for the present metallographic needs. Strangely enough, in spite of their importance, the alloys of iron, carbon and manganese apparently have not been investigated in the same systematic manner, and so far as is known, no three-component equilibrium diagram for this system is available. Even iron-carbon-nickel alloys³ have been studied rather more thoroughly; for these the solidus and liquidus surfaces have already been determined, but the solid transformations in this, as in the manganese system, have not been reported systematically.

The present paper deals with the constitution at equilibrium of a series of 36 iron-carbon-manganese alloys of commercial purity limited by 1.5 per cent carbon and 15 per cent manganese, a range of compositions including most of the manganese steels. The temperature range of melting has not been determined, nor has the high-temperature (delta iron) ferrite equilibrium been included in the study, it being considered that the more important characteristics of the manganese steels are their ordinary transformations in the solid state. The delta iron region is almost certain to be a small tetrahedron not very different in magnitude or contour from that in the iron-carbon-nickel diagram. It is probably true

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¹ V. N. Krivobok and M. A. Grossmann: A Study of the Iron-Chromium-Carbon Constitutional Diagram. *Trans. Amer. Soc. Steel Treat.* (1930) 18, 760.

T. Murakami, K. Oka and S. Nishigori: The Transformation and Constitution of High-Chromium Steels. *Tech. Repts.*, Tôhoku Imp. Univ. (1930) 9, No. 3, 405.

A. Westgren, G. Phragmén and T. Negresco: On the Structure of the Iron-Chromium-Carbon System. *Jnl. Iron and Steel Inst.* (1928) 117, 383.

² S. Takeda: A Metallographic Investigation of the Ternary Alloys of the Iron-Tungsten-Carbon System, Pts. I, II, III. *Tech. Repts.* Tôhoku Imp. Univ. (1931) 9, No. 4, 433.

³ T. Kasé: On the Equilibrium Diagram of the Iron-Carbon-Nickel System. *Sci. Repts.*, Tôhoku Imp. Univ. [I] (1925) 14, No. 2 174.

that more frequent use is made of a knowledge of the general trend of the reactions in the solid as its composition changes than of any scattered single measurements, no matter how accurate the latter may be. Accordingly, only sufficient compositions have been studied to establish the various temperature zones for the four phases so far found in the system, and to show with reasonable accuracy the nature of the effect of the elements carbon and manganese upon the critical temperatures. The system reveals no very unexpected idiosyncrasies; accordingly the three-dimensional diagram shows mainly smoothly curved or warped surfaces with easily estimated intersections. It is expected that the equilibrium

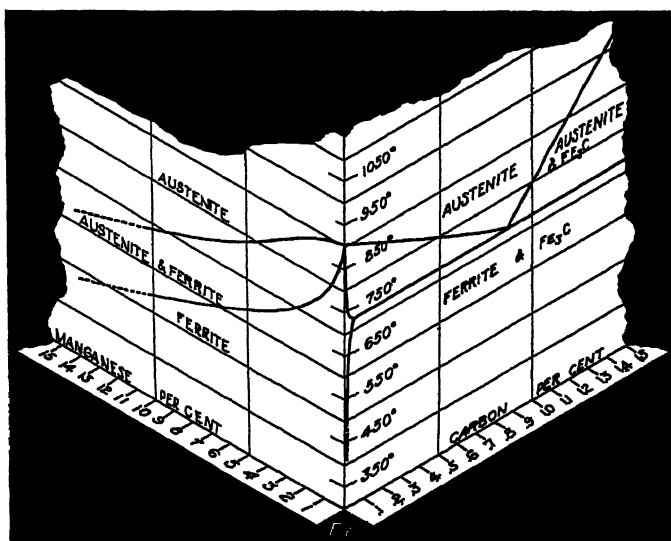


FIG. 1.—DIAGRAM OF THE TWO BINARY SYSTEMS IRON-CARBON AND IRON-MANGANESE.

diagram offered here will serve as an aid in the interpretation of individual behaviors which may be observed in the future, and it may thereby be adjusted to higher precision as more exact work is reported from time to time.

In this connection it should be mentioned that the attempt at construction of a ternary diagram implies knowledge of the pertinent binary diagrams. In Fig. 1 are shown the two binaries involved in the part of the iron-carbon-manganese system engaging present attention. In brief, the task attempted here is that of supplying the information necessary for constructing the interior of the solid diagram included between these two limiting planes. Actually only one of the two binary diagrams demanded here is really well known. The amazingly precise and thorough work now being conducted by the Bureau of Metallurgical Research, Carnegie Institute of Technology under the directorship of Dr.

F. M. Walters, Jr., has been reported,⁴ but as yet the iron-manganese equilibrium diagram has not been published. The present paper has been offered in the hope that presently the equilibria in pure alloys of iron and manganese will be reported upon up to at least 15 per cent manganese, and that these results may be used to fix the zero-carbon ordinates of this ternary diagram. However, the results already furnished from that source have been examined critically and the dilatometric data therefrom have been utilized to construct a provisional iron-manganese diagram which may serve to mark out the zero carbon limits for these iron-carbon-manganese diagrams. The extreme low-carbon compositions, therefore, will be subject to revision as to phase boundaries when the pure iron-manganese equilibrium diagram is well established.

REPRESENTATION OF THREE-COMPONENT SYSTEMS

In general, the construction of any graphic representation of the constitution at equilibrium of a three-component system presents characteristic difficulties, which, however, may be overcome by the use of the triangular system of plotting compositions and the use of a third dimension for indicating temperature. The domains of phases then become solids of which the "thickness" is temperature range of stability and the "width" and "breadth" are composition ranges in terms of two of the components respectively. The concentration of the third is obviously 100 per cent less the sum of the other two. Thus, in reality, any three-component composition is portrayed in terms of two, since the third is really a function of the other two. Practically, for construction, vertical rods appropriately marked or colored in bands serve to denote the temperature zones of stability for the various phases for the several compositions, each of which is represented by a point in the composition base upon which the vertical is erected. The surfaces connecting corresponding points on the verticals are then the phase boundaries of the ternary system. Furthermore, the triangle of three-component representation (the so-called Roozeboom diagram which, however, was originated by Willard Gibbs) need never be an equilateral one, and for studies of compositions near one of the pure components, a right angle is in many ways preferable to the sixty-degree angle. This becomes particularly advisable when the one alloying element is studied over a narrower range than the other, as in the present case.

⁴ Carnegie Inst. of Tech. Metallurgical Board *Bull.* 101. Alloys of Iron, Manganese, and Carbon: Pt. I. Preparation of Alloys, by F. M. Walters, Jr.; Pt. II. Thermal Analysis of the Binary Alloys, by F. M. Walters, Jr. and C. Wells; Pt. III. An X-ray Study of the Binary Iron-Manganese Alloys, by M. Gensamer, J. F. Eckel, and F. M. Walters, Jr.; Pt. IV. A Dilatometric Study of Iron-Manganese Binary Alloys, by F. M. Walters, Jr. and M. Gensamer. Bureau of Metallurgical Research, Carnegie Inst. of Tech. Series of four papers presented before the Amer. Soc. Steel Treat., Boston, Mass., Sept., 1931.

But for presentation on the printed page such solid diagrams are not manageable. The alternative is to slice up the solid diagram with its various internal surfaces into a sufficient number of sections and to present these separately so that the sweep of the surfaces may be inferred. The sections will be just as accurate as the solid diagram, and may be cut in any direction desired, but the customary and more useful sections are either cut parallel to the plane of zero concentration of one of the components or are cut horizontally, parallel to the composition plane through isothermal intercepts. In general, it may be said that, while all have been used, the set of parallel cuts to be chosen should not be even approximate parallels to the principal phase boundary surfaces of the diagram. The more nearly normally such surfaces are intercepted, the more lucid the representation of their traces.

A word of caution in respect to the use of successive vertical sections of ternary diagrams may not be out of place. Such plane two-dimensional diagrams often superficially resemble binary diagrams, but they are not even pseudobinaries, and may not be used in the same way. No knowledge of the proportions or compositions of two phases in equilibrium is conveyed or implied by such sections. The points representing the compositions of the phases present are in general not in the plane of the diagram, but are always located on some isothermal straight line passing through the composition of the alloy as a whole. When three phases are in equilibrium it is still more obvious that the plane-section diagram cannot show the proportion or composition of the phases. The section diagram does, however, show the number and nature of the phases present at any temperature for any total composition shown in the plane. It is to be noted that while in two-component systems only nonvariant points may exhibit three phases simultaneously at equilibrium, it is common to find three phases in equilibrium in three-component systems over a variety of compositions and temperatures.

All these circumstances are encountered in presenting the equilibria of the iron-carbon-manganese system and, in particular, the three-phase region appears with considerable practical significance.

THE SYSTEM IRON-CARBON-MANGANESE

This portion of the paper will show various sections of a part of the solid equilibrium diagram, the major dependence being placed upon the use of constant-manganese, variable-carbon sections with temperature as ordinate. As will be discussed, the data are presented without reference to the variable silicon content present as a sequel to deoxidation. Familiarity with the usual iron-carbon diagram serves here to make the presentation easier and, it is hoped, the interpretation as well. A convention has been adopted to designate the degree of accuracy with which the work was accomplished. Solid lines indicate phase boundaries

fairly well established, with an accuracy of about $\pm 7^{\circ}$ C. (12° F.); lines formed of long dashes signify some doubt as to temperature, although equilibrium in all cases is implied, perhaps $\pm 10^{\circ}$ C. (18° F.); dotted lines indicate regions where the condition of equilibrium is difficult to secure, and may not have been reached precisely. In the compositions of the very low-carbon alloys the same dotted lines have been employed to indicate the transformation temperature which may be revised with further reports.

In the section of the paper following thereafter, the methods, materials, and equipment are discussed briefly. While the microscope was depended upon as the chief source of information and no less than 620 specimens were examined, only a few typical photomicrographs are shown. It is believed that, however picturesque they may be, there is little or nothing to be gained by reproducing photomicrographs of the basic structures—martensite, ferrite, ferrite with spheroidized carbides, austenite with carbide plates, etc., etc.—in connection with an equilibrium diagram, since these all too familiar constituents may now be described fully in a word and the very slight differences between these same well-known constituents as formed in one or another steel are all matters wholly unrelated to equilibrium, and depend almost entirely upon either grain size or particle coalescence. The authors themselves, however, find these matters extremely entertaining and discovered early in the investigation the need for the most careful preparation of microscopic specimens and the aid to interpretation offered by precise classification of the occurrences and distributions of constituents.

Broad Aspects of the Equilibrium Diagram.—As has been predicted, the addition of moderate amounts of manganese (less than about 10 per cent) to iron-carbon alloys introduces no serious complexities to the comparatively simple iron-carbon diagram. Only three major influences are manifest: (1) a small and systematic change in the temperature zones of stability for the phases, (2) a very great decrease in the rate of reaction by which one constituency changes to another when the temperature is raised or lowered through a critical point, and (3) an influence of manganese permitting the simultaneous appearance along with austenite of the phases, ferrite and carbide, otherwise mutually incompatible in the presence of the third phase, austenite. That no new phases are formed by adding such moderate amounts of manganese is merely a corollary of the three basic behaviors of manganese; (1) it is moderately soluble in alpha iron, (2) it is even more soluble in gamma iron, and (3) its carbide Mn_3C is isomorphous with, and so dissolves in, Fe_3C .

The minimum temperature at which the first austenite makes its appearance upon heating is lowered consistently by manganese, regardless of the uniform carbon content under consideration. In this respect nickel

and manganese are very similar. On the other hand, with constant manganese content, in a series of alloys with increasing carbon content, it is found that this critical temperature is raised with the first substantial increases in carbon (up to several tenths of one per cent)—a striking circumstance, demanded however by the greater tendency for the separation of Mn_3C than for Fe_3C , or in other words, the greater stability of Mn_3C . Other investigators have already found that manganese elects to combine with the carbon to the partial exclusion of iron, in a proportion exceeding its relative concentration in the alloy as a whole; the rise in the lowest critical point with carbon content is therefore predictable.

Turning now to the low-carbon alloys containing more than about 10 per cent manganese, it is found that the critical points have been depressed to a temperature below which neither grain growth nor diffusion proceeds at a practicable velocity, and accordingly transformations on cooling either may not occur at all, or the austenite decomposition (generally only partial) on cooling must proceed by the mechanism of martensite formation in which neither grain growth nor diffusion need occur. In any event, extremely long time is required to cause even microscopically visible particles of any newly formed phase to develop at the temperature of these transformation ranges. In this region, therefore, the accuracy is least. With higher carbon content, however, the reactions, and the subsequent coalescence, take place with a velocity permitting some microscopic study, although only after a few weeks at temperature, and the accuracy of observations is improved.

The Epsilon Phase.—It is in this high-manganese low-carbon range of composition that the phase characterized by a hexagonal crystal structure is observed. It seems advisable to complete a discussion of this unique occurrence at this early point in the interest of avoiding confusion in connection with the later inquiry into the other compositions of the system. The phase was designated by the Greek letter ϵ by its discoverer, Schmidt,⁵ and has been described also by Öhman,⁶ Scott,⁷ and Gensamer.⁸ Whether or not it is a stable phase and therefore properly designated on an equilibrium diagram seems to be an open question.

The persistence of this phase strongly suggests that it may be stable, but a number of circumstances point otherwise. It is partly removable in some alloys by cold work and subsequent prolonged heating just below

⁵ W. Schmidt: X-ray Investigations of the Iron-Manganese System. *Archiv. f. d. Eisenhüttenwesen* (1929) 3, 293.

⁶ E. Öhman: X-ray Investigations of the Iron-Manganese System. *Ztsch. f. physik. Chem.* (1930) 8, 81.

⁷ H. Scott: Transformational Characteristics of Iron-Manganese Alloys. *Trans. A. I. M. E., Iron and Steel Div.* (1931) 284.

⁸ M. Gensamer, J. F. Eckel and F. M. Walters, Jr.: Alloys of Iron, Manganese and Carbon, III.—An X-ray Study of the Binary Iron-Manganese Alloys. Presented before the Amer. Soc. Steel Treat., Boston, Mass., Sept., 1931.

the lowest critical point. It is not formed at all in some austenitic alloys which, nevertheless, with cold work may be rendered somewhat ferritic. It forms principally in alloys which transform also partly into ferrite by the martensitic mode of transformation. In this case, the total volume change with transformation (and hence the internal stress set-up) is small; for martensite is voluminous and epsilon is dense. The mode of dispersion of the two phases is clearly in tiny platelets, in which the volume compensation may be nicely adjusted.

Perhaps one may consider that epsilon is a stable phase based on a compound of iron and manganese, stable only at the lower temperatures; but more probably it is an unstable condition quite comparable with martensite. Explaining the second possibility, one may visualize how slight the atomic motions need be to form either martensite or epsilon out of austenite. Indeed, one may wonder how it comes about that carbon-bearing austenite elects to form the tetragonal martensite instead of the hexagonal epsilon. When austenite transforms to martensite, a body-centered tetragonal (ratio 1.414 identical with the face-centered cubic crystal) changes into an almost cubic (ratio not over 1.06) body-centered tetragonal crystal merely by a family of rectangles 2.546 Å. by 4.420 Å. shifting to a similar family, in this case now approximately 2.860 Å. by 4.047 Å. This product is martensite. To produce epsilon from austenite, the change is even simpler. Austenite may be represented as the orthodox face-centered cubic or body-centered tetragonal crystal, but may be just as well regarded as rhombohedral ($a = 2.546$ Å., ratio = 2.4495, interplanar distance $h/3 = 0.8165$ Å.). In this crystal the basal planes are all equilateral triangular patterns of atoms. The successive layers are so placed that each atom lies at the center of the triangles of the layer below. But there is always a choice of two positions for each successive plane of triangles which fulfill this requirement. In austenite the choice is made in such a manner that only each third layer is in exactly the same position. In the close-packed hexagonal structure of epsilon these same layers of basal planes persist as before, except that now the choice as to alternate position is such that every second layer is precisely alike. Hence the change from austenite to epsilon involves only a slight shift (or rotation) in two-thirds of its basal planes, accompanied by a slight general contraction ($a = 2.53$ Å., ratio = 1.61, interplanar distance $h/2 = 0.805$ Å.). The greatest distance of shift for any atom is only 1.47 Å. during the austenite-epsilon transformation. In any event, when the austenite of the low-carbon high-manganese steels transforms, it does so by either one, or more usually both, of these slight atomic rearrangements, neither one of which requires any grain-boundary migration or any diffusion, and is then a mixture of epsilon, martensite and residual austenite. At a temperature at which either of these two new crystal forms, ferrite or epsilon, could coalesce into sizable

masses or grains, the austenite is already stable again, and as a result, the problem of determining whether or not epsilon is a stable phase becomes extremely difficult. At the moment, the view that epsilon is a transient structure similar to the slightly tetragonal martensite of carbon steels seems most acceptable, and certainly the most compatible with our knowledge of low-temperature transformations. The most significant observation is that with higher carbon content, which raises the transformation point to high enough temperatures to avoid the martensitic mode of transformation, these high-manganese alloys transform from the austenitic form to the pearlitic form with the production of no epsilon phase.

The foregoing detailed consideration of the epsilon phase is introduced in order to provide a basis for the dismissal of the matter of this phase from the contemplation of the usual transformation points of the system. Only at temperatures below that for the existence of some austenite is this phase formed and it is therefore entirely possible to regard it as an alternative form of low-carbon martensite, which, indeed, it may almost supplant in the alloys containing manganese to the extent of about 26 per cent, well beyond the composition range of this inquiry. While it may be a permanently persistent phase in so far as all known methods of inducing equilibrium are concerned, the view that it, rather than ferrite, is the final low-temperature form of ultimate stability is a possibility, but a remote one in view of the fact that cold work, followed by heating just below the lowest transformation point, reduces its proportion. At any rate, the following presentation of the equilibrium diagram need not consider it as other than an accompaniment of the ferrite produced out of the austenite as it transforms at these relatively very low temperatures.

THE SECTIONAL DIAGRAMS

Each of the diagrams of Figs. 2, 3, 4, 5, 6, 7 and 8 is a uniform-manganese, variable-carbon section of the three-dimensional diagram, and shows which phases are at equilibrium at various temperatures as carbon is increasingly present in the iron-manganese alloy designated. The diagrams do not, however, give any information as to the composition or proportion of any phase in the heterogeneous fields. In order to save space, the constituents present are designated in all diagrams by initials: *A*, austenite; *F*, ferrite; *C*, carbide; ϵ , epsilon; *M*, martensite; *T*, troostite; *P*, pearlite; etc. The sections chosen correspond to manganese levels of unequal distribution instead of even manganese percentages, as might have been expected. This choice of sections is made as a result of the particular assortment of compositions studied, which clustered near these several concentrations of manganese. By plotting a section of the solid diagram near these manganese planes representing mean compositions for the groups, the degree of interpolation becomes

very slight and the accuracy of each diagram is essentially that of the temperature measurements. In Fig. 3 it becomes apparent that even 1 per cent manganese is able to produce a detectable temperature range for three-phase equilibrium, particularly in the hypoeutectoid steels. This

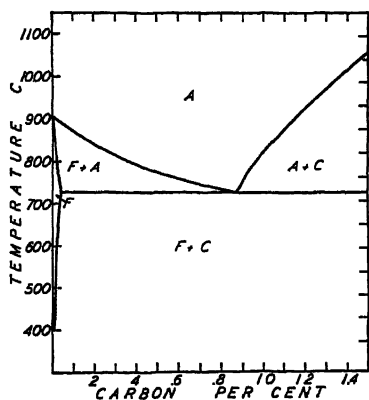


FIG. 2.

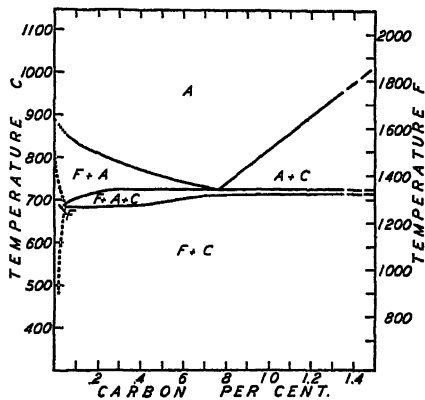


FIG. 3.

FIG. 2.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 0 PER CENT MANGANESE.

FIG. 3.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 1.0 PER CENT MANGANESE.

zone must occupy a wedge-shaped space and just vanish at zero manganese, where the zone is then the single eutectoid horizontal, or A_1 . The higher manganese alloys represented in Figs. 4, 5, 6, 7 and 8 show the gradual widening of this zone of three stable constituents. One note-

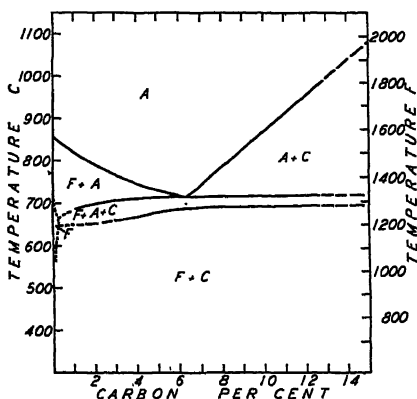


FIG. 4.

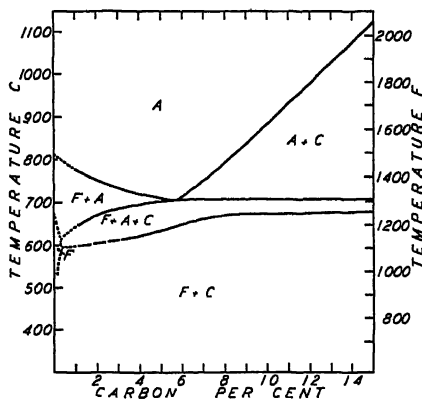


FIG. 5.

FIG. 4.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 2.5 PER CENT MANGANESE.

FIG. 5.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 3.8 PER CENT MANGANESE.

worthy circumstance is the gradual flattening and tilting of the three curves involved immediately about the eutectoid point. As with higher manganese content the three-phase zone becomes wider in temperature, the three lines approach one another more and more nearly, for the

reason that the upper limit of the three-phase zone is bounded by a line which is now in fact nearly a continuation of the other two lines. Thus, for the hypereutectoid alloys the middle line marks the disappearance of ferrite just as does the topmost line of the hypoeutectoid side of the diagram. Similarly, the middle line in the hypoeutectoid region is nearly a continuation of the topmost line of the hypereutectoid region, marking as it does the disappearance of carbide. The reason this close approach of the three curves is so much more marked in the high-manganese alloys than in the lower manganese alloys nearer the two-component carbon steels is that with a large three-phase zone the entire region around the eutectoid point is nearly pure austenite, above and below; hence the solubility curves which are plotted have to do with nearly the same solvent instead of very different ones.

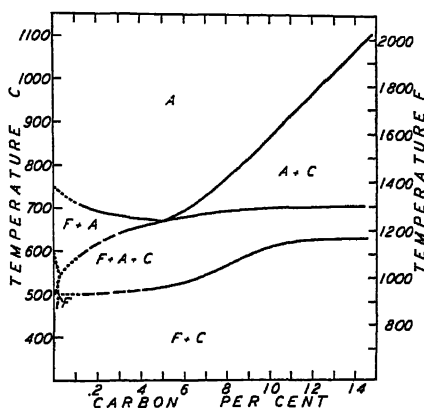


FIG. 6.

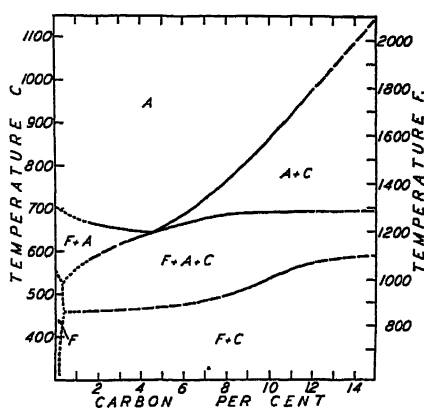


FIG. 7.

FIG. 6.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 6.5 PER CENT MANGANESE.
 FIG. 7.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 9.0 PER CENT MANGANESE.

At first glance, a plot representing a eutectoid point at a temperature higher than some points in a curve denoting the solubility of one of the phases involved, as in Fig. 8, may appear absurd. It is, however, entirely correct according to experimentation, and appears questionable only because of the tendency to regard a section of the solid equilibrium diagram as a binary diagram, which of course is erroneous. In Fig. 8 this is particularly marked, but it will become clear that there is nothing inconsistent in this section when it is realized that the eutectoid composition of 13.3 per cent manganese and 0.385 per cent carbon is in reality a eutectoid between a ferrite of very low manganese content, not represented in the diagram at all, and a carbide very rich in manganese, also not in the diagram. If one is unable to accept this circumstance, it will become clear if he will construct a small portion of the dihedral angle formed by the two solubility surfaces involved and draw a suitable

trace thereon, representing the manganese-lean ferrite and the manganese-rich carbide, and, of course, the intermediate austenite. If other proof were lacking, this section alone of the solid diagram would prove the greater stability of the manganese carbide, and its preferred formation to the partial exclusion of iron carbide. At the risk of introducing too much detail, it may be well to invite attention to the fact that the lowest line in each of the diagrams is fairly horizontal at low carbon, rises rapidly with the next additions, and is finally nearly horizontal over a range of high-carbon concentrations. These three stages of the lowest critical range shift to higher carbon content with increasing manganese. This may be interpreted as indicating certain important behaviors as to carbide formation. If we consider the formation of carbide by the intro-

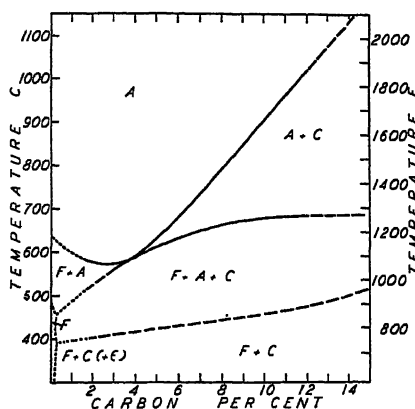


FIG. 8.

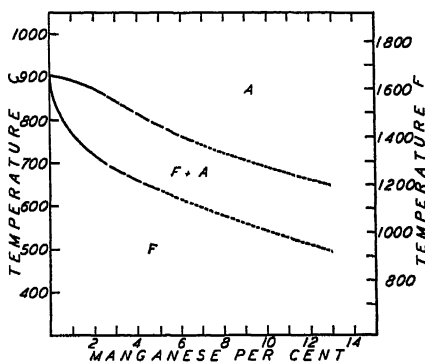


FIG. 9.

FIG. 8.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 13.3 PER CENT MANGANESE.

FIG. 9.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 0 PER CENT CARBON.

duction of successive amounts of carbon to the iron-manganese alloys, the first carbide to form will be very rich in manganese; perhaps nearly wholly Mn_3C . But manganese is thus soon exhausted and, being no longer very available, a carbide of diminishing manganese content is therefore formed with further additions of carbon, until finally the carbide is essentially Fe_3C . It may be observed that the "bend" in the curve for the lowest critical point moves gradually to the high-carbon side of the diagrams as the manganese content increases. This circumstance reflects the preferred formation of Mn_3C , which does not so rapidly exhaust the manganese in the high-manganese alloys. In this interpretation it must be borne in mind that the lowering of the low critical point is dependent upon the manganese remaining in solution in the ferrite rather more than upon the composition of the carbide with which it is in contact. The impoverishment of the ferrite, with respect to its manganese, by carbide formation raises the critical temperature sharply.

The phase boundaries in the diagrams mark off the critical points of the several steels in the sense of Howe's⁹ "Ae points," but a difficulty exists in assigning the usual numbers to the letter "A." Presumably the temperature at which the steels just become wholly austenitic at equi-

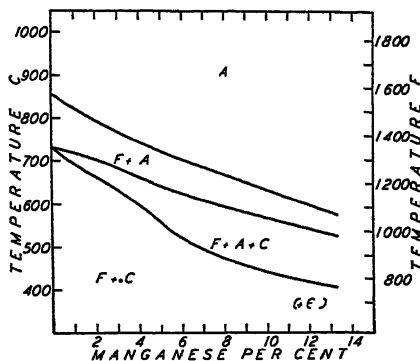


FIG. 10.

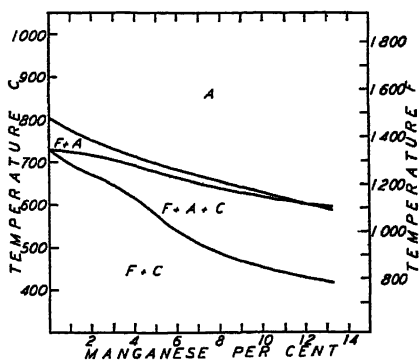


FIG. 11.

FIG. 10.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 0.2 PER CENT CARBON.
FIG. 11.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 0.4 PER CENT CARBON.

librium would be designated as Ae_3 , or Ae_{cm} , but Ae_1 is inadequate for representing two critical temperatures of transformation, such as are found in the three-component steels. One might possibly denote the lowest temperature of austenite appearance as Ae_{1L} (low), and the temper-

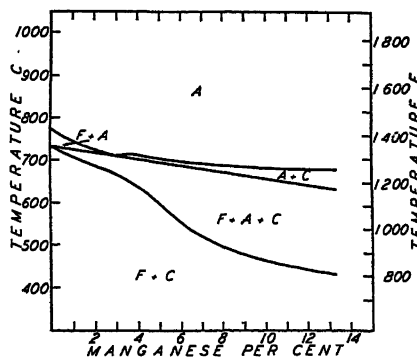


FIG. 12.

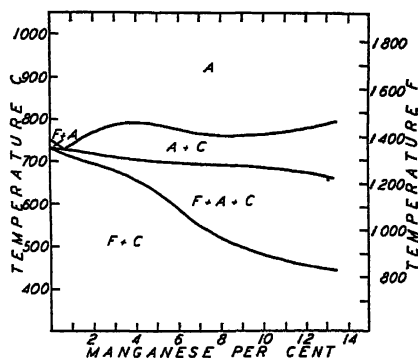


FIG. 13.

FIG. 12.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 0.6 PER CENT CARBON.
FIG. 13.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 0.8 PER CENT CARBON.

ature of the disappearance of the non-proeutectoid constituent as Ae_{1M} (middle), but the naming of the critical temperatures is avoided in this paper. Aside from what the critical temperatures may be called, the fact remains that alloy steels in general do not possess a single-tempera-

⁹ H. M. Howe: The Metallography of Steel and Cast Iron. McGraw-Hill Book Co., New York, 1916.

ture critical point upon heating for both the disappearance of ferrite or carbide (hypereutectoid or hypoeutectoid steels respectively) and the formation of austenite. Therefore the designation A_1 for such steels

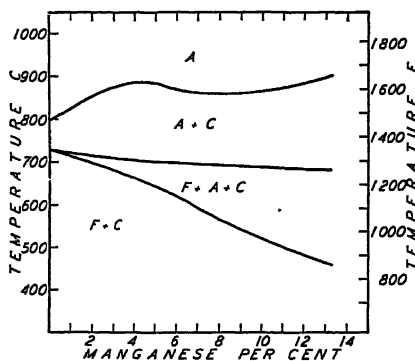


FIG. 14.

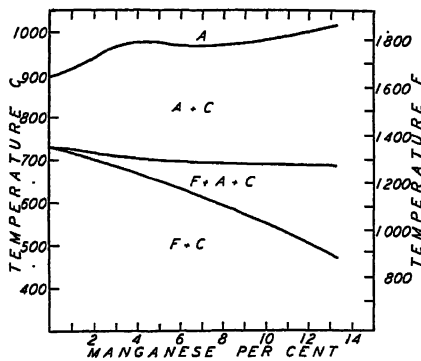


FIG. 15.

FIG. 14.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 1.0 PER CENT CARBON.
FIG. 15.—SECTION OF THE THREE-DIMENSIONAL DIAGRAM FOR 1.2 PER CENT CARBON.

carries a degree of inaccuracy depending upon the amount and nature of the alloying element. It is sometimes convenient, however, to regard low-alloy steels as though they were binary alloys, but in that case the exact meaning of any critical points mentioned should be clearly defined.

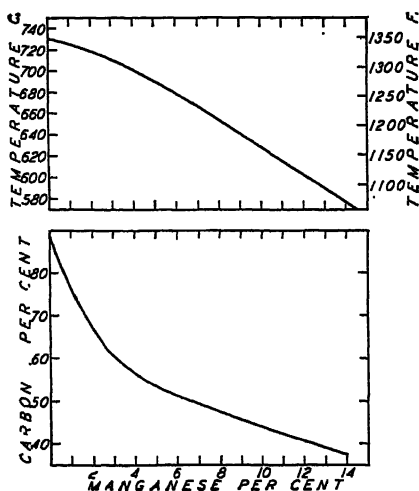


FIG. 16.—TEMPERATURE AND CARBON CONTENT OF EUTECTOID AS A FUNCTION OF MANGANESE CONTENT.

A set of sectional diagrams, in each of which the carbon content is constant and manganese is variable, are shown in Figs. 9 to 15. These less familiar looking charts are derived from the constant manganese sections and are of the same accuracy. In the use of these charts for interpolating the transformation points of other intermediate alloys, care should be exercised with compositions near the eutectoid, for in this region the curves show abrupt breaks. Accordingly, Fig. 16 is introduced to show the eutectoid temperature and composition for the system as inferred from the data obtained.

THE METHOD

In general the critical points were located by the microscopic appearance of suitable forged specimens after quenching from various tempera-

tures maintained sufficiently long to induce substantial equilibrium. The phases developed at equilibrium at the various elevated temperatures may not be preserved by quenching, later simply to be examined and identified under the microscope. Only with the very highest manganese concentrations studied is this optimum condition realized. However, it is just as satisfactory if the quenched structure marks out the masses of the original phases and provides clues for their recognition. For example, in these steels, austenite at equilibrium above, say, 750° C. (1380° F.) will, upon quenching, either appear as such with twinned grains, or, more often, as martensite, while the carbide will easily be recognizable either as plates, lamellae or spheroids, depending upon its history. Ferrite will also be recognizable by the difference in surface texture in contrast to the acicular markings of the martensite. Most of the martensite retains generous proportions of austenite, but this offers no complications.

Each specimen was also studied by means of X-ray crystallography, but in general this evidence is of little value except as regards occasional corroboration. Approximate measurement of magnetic permeability by a crude magnetometer was about as useful. One could not, for example, estimate, by the X-ray or magnetic methods employed, ferrite accompanied by martensite with sufficient accuracy to aid materially in constructing the equilibrium diagram. For the low-carbon alloys, the dilatometer provided some information on specimens which had previously been brought to the ferritic state by cold work, refrigeration or long-time heating at moderate temperatures, or combinations of all these treatments.

The Alloy Specimens.—The 36 steels melted especially for this study were supplied by the Physical Laboratory, Illinois Steel Co. They were produced in a small 250-lb. arc furnace, by careful practice approaching that employed for tool steels; cast into 40-lb. ingots, generously cropped and forged into $\frac{1}{2}$ -in. square bars. All compositions forged without any difficulties whatever. One heat showing a center segregation was discarded. The 98.5 per cent reduction of cross-section during forging appeared to eliminate substantially all traces of the ingot segregation due to coring. Some slight banding was noticed, but of a type interfering very little with the quantitative estimation of constituents, which, in any event, was made on the cross-section. Bars were selected that were almost entirely free from seams.

The typical specimen was a $\frac{1}{2}$ -in. cube, but wherever further work was to be done on a heat-treated specimen, longer sections were utilized and cube sections cut therefrom for subsequent treatments. The removal of $\frac{1}{16}$ in. of metal by grinding sufficed to permit observation on metal free from decarburization even after the most severe treatments.

In the study of a ternary system of this sort, one is usually confronted by the question of which of two procedures to follow. On the one hand,

small ingots of pure material may be made, and the results, if accurate, will be representative of the genuine three-component steels and have maximum value for precise reference. Such data are sought for inclusion in critical tables of physical constants. On the other hand, such data will not represent commercially possible alloys and are therefore not of greater utility than those relating to *impure* alloys which differ no more from the commercially possible metal. Obviously, both sorts of data are needed and both should be welcomed whenever made available. In the present case the authors have believed that the item of immediate usefulness was paramount, and in view of certain circumstances to be mentioned, they doubt that there is any considerable disparity between the diagram for these alloys and that of the pure metals. The manganese alloys, except as forged or otherwise worked thoroughly to an unusual degree, retain a segregation of the microscopic sort resulting from coring. It has been observed¹⁰ how extremely slowly this inhomogeneity is effaced from the cast metal. For this reason, unless rather large ingots can be cast and forged very considerably, impractically long heatings at temperatures near the melting point may be required to produce a homogeneous austenite out of which the various phases may form. Pure elements melted together so as to preserve this purity usually will prove too costly to permit large ingots. When possible, however, this is the preferred procedure for precise data. But other difficulties may result from the presence of voids in ingots which have not been degasified, either by melting in vacuo, or by silicon additions. Large melts are difficult to handle in vacuo. The pure metal studies are therefore the more praiseworthy.

A few scattered tests indicate that the presence of a small residual silicon content, even up to 0.25 per cent, in steels carrying substantial amounts of manganese, nickel, or even chromium alters the critical points by a rather small amount—probably well under 10° C. (18° F.). This shift in critical temperature is toward higher temperatures universally and therefore is not significant in the trends of the system. The silicon effect upon critical points is not greatly unlike a systematic error in the thermocouple readings made during the study. The temperatures discovered will apply, of course, directly to the vast majority of commercial steels which in general would contain similar residual silicon after deoxidation.

The alloys of the present study have the compositions listed in Table 1.

The Heat Treatments.—The authors have held to the viewpoint that for the purpose of bringing alloys to the condition of equilibrium the method of “slow cooling” cannot by nature be the most rapid or efficacious procedure. The inferiority of the “slow-cooling” practice becomes more and

¹⁰ B. M. Larsen: Effect of Manganese on Distribution of Carbon in Steel. U. S. Bur. Mines *Tech. Bull.* 466 (1929).

TABLE 1.—*Analyses of Alloys Studied*

Heat No.	Composition, Per Cent				
	Carbon	Manganese	Silicon	Sulfur	Phosphorus
1	0.06	1.26	0.14	0.010	0.013
2	0.24	1.07	0.04	0.009	0.013
3	0.47	0.88	0.05	0.008	0.021
4	0.66	0.87	0.09	0.007	0.026
5	0.80	0.88	0.14	0.006	0.027
31	1.39	0.98	0.01	0.020	0.012
6	0.07	2.42	0.13	0.008	0.015
7	0.27	2.26	0.15	0.008	0.018
8	0.53	2.21	0.14	0.008	0.025
9	0.86	2.58	0.21	0.007	0.031
10	1.24	2.86	0.27	0.007	0.038
11	0.07	4.24	0.29	0.011	0.025
12	0.25	3.92	0.27	0.008	0.026
13	0.54	3.72	0.31	0.008	0.027
14	0.75	3.52	0.39	0.008	0.029
15	0.90	3.40	0.48	0.008	0.031
33	1.28	4.60	0.01	0.013	0.020
32	1.50	3.92	0.03	0.014	0.015
16	0.10	6.71	0.06	0.009	0.034
17	0.30	6.53	0.07	0.007	0.033
18	0.60	6.45	0.14	0.008	0.035
19	0.92	6.48	0.19	0.013	0.037
20	1.20	6.19	0.26	0.012	0.043
34	1.64	6.48	0.01	0.011	0.023
35	0.10	8.46	0.09	0.012	0.046
21	0.14	10.85	0.19	0.010	0.039
22	0.30	9.10	0.19	0.008	0.040
23	0.61	9.10	0.34	0.013	0.054
24	0.92	9.10	0.25	0.014	0.048
25	1.11	9.05	0.40	0.012	0.059
26	0.09	13.49	0.07	0.011	0.057
27	0.29	13.05	0.27	0.007	0.054
28	0.54	13.39	0.05	0.010	0.066
29	0.78	13.59	0.07	0.011	0.052
30	0.94	12.87	0.11	0.010	0.043
36	1.33	14.67	0.09	0.007	0.040

more pronounced as greater sluggishness is induced in the steel by higher and higher alloy content. For this reason the equilibrium condition even at the lowest subcritical temperatures has been brought about in the present investigation by maintaining the specimen at constant temperature for a length of time sufficient *by actual test* to complete the reactions.

A preliminary examination located the critical points in a general way, and for this purpose one specimen of each steel was properly heated at each temperature level, selected at 25° C. (45° F.) intervals. By

experience it was decided to extend the 25° C. (45° F.) intervals over a total range limited by reasonable expectancy of any critical points. Later a second series of similar specimens was heated at temperatures midway between the temperature levels of the first series. Thus, a phase would always be present at some certain temperature and absent entirely at the next temperature level just 12.5° C. (22° F.) above or below, fixing one point on a phase-boundary line to within about $\pm 6^\circ$ C. (11° F.). As will be seen later, in many cases the accuracy was somewhat better than this. Specimens for all precise phase end-point determinations, for estimations of the carbide-disappearance temperature and for all low-temperature work, were given a special homogenizing treatment at high temperature before the heating for equilibrium was begun. In some cases the homogenizing treatment rendered the microscopic work more difficult.

Heating for the studies at the highest temperatures, and therefore for the shortest times, 900° to 1200° C. (1650° to 2200° F.) was accomplished in a carborundum resistor muffle, while the medium temperatures were applied in lead pots, all automatically controlled to about $\pm 5^\circ$ C. (9° F.) by Wilson-Maeulen controllers. For the very long heatings at low temperatures up to about 600° C. (1110° F.) the specimens were

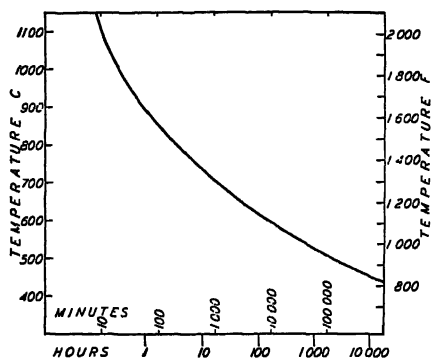


FIG. 17.—ESTIMATED TIME REQUIRED FOR EQUILIBRIUM AT VARIOUS TEMPERATURES.

protected in heat-resisting alloy boxes heated in nickel-chromium resistor muffle furnaces automatically controlled.

Period Required at Temperature for Equilibrium.—The method described herein consists of bringing the alloys substantially to conditions of equilibrium at a variety of constant temperatures. This condition can be assured only when some change from the starting condition is brought about in a reasonable interval of time and

when considerably longer maintenance of the temperature produces no further change in proportion of the constituents. This test for equilibrium was employed in the present study. Not all specimens, however, were thus verified for equilibrium. It was found that for equivalent carbon content low-manganese alloys attained equilibrium in shorter time than the higher manganese alloys, and that over certain ranges of composition high-carbon alloys reached a constant constitution earlier than the lower carbon alloys. Accordingly, a large number of specimens could be treated simultaneously for one time interval, which was adequate for the most sluggish and more than adequate for the others at the particular temperature level.

The time-temperature curve of Fig. 17 shows the approximate period required to insure complete equilibrium in the alloys other than those of low carbon and high manganese content whose critical points lie below 500° C. (930° F.). For these, cold work followed by long low-temperature heatings brought about the transformation of austenite to a degree suitable for subsequent dilatometric exploration. The figures plotted for these alloys are of the least accuracy of the series.

Microscopic Estimation of the Phases.—The specimens were polished by the usual procedure, care being taken to insure removal of sufficient metal by grinding to present for final polishing a surface free from decarburization or “de-manganization.” In general, repeated applications to the magnesia abrasive with repeated intervening etchings were found to improve the preservation of some of the finest pearlite structures which are resolved only with the 90x, 1.30 NA objectives. A variety of etching agents were employed for the various differentiations, but the alcoholic nitric acid solution could be relied upon for the best results after some experience had been gained. In a few cases, carbide blackening etches with sodium picrate were useful and the clean-cut etch of aqua regia: glycerin was at first used somewhat for the specimens which were largely austenitic.

The method of visual estimation with a ruled micrometer eyepiece gave the best quantitative measure of constituent proportion. A photomicrograph may be printed on paper and the constituents may then be cut out and weighed for very precise work, but this method was used only for checking on the other method. After many estimations, it was found that sufficient skill may be acquired in direct estimation without any accessories; rarely indeed would any four observers differ by 10 per cent in the estimation of proportions. The average of three or four closely agreeing opinions was recorded as final. The estimation of austenite and martensite, pearlite or ferrite was always fairly satisfactory, but carbide plates could not be estimated with any great degree of precision. Of course, for the purposes of determining the temperature limits of the phases, the presence or absence of carbide is adequate.

Figs. 18, 19 and 20 show the three characteristic microstructures encountered most frequently in the examination of the specimens; they represent the structures resulting from the equilibrium respectively of ferrite with austenite, carbide with austenite and austenite with ferrite and carbide. Excellent photomicrographs by Lucas, showing the typical association of carbide plates, austenite and pearlite in the partly transformed austenite of 12 per cent manganese steel with the high carbon content of the Hadfield range, are presented in Figs. 30 to 40 of J. H. Hall's Howe Memorial Lecture of 1929.¹¹ While the specimens employed

¹¹ J. H. Hall: Studies of Hadfield's Manganese Steel with the High-power Microscope. *Trans. A. I. M. E., Iron and Steel Div.* (1929) 407.



FIGS. 18-20.—CAPTIONS ON OPPOSITE PAGE.

for the Hall-Lucas photomicrographs were clearly not brought to equilibrium, the structures revealed are nevertheless quite representative of the three phases at equilibrium at an appropriate temperature. Krivobok¹² has also photographed well formed pearlite in Hadfield steel.

Figs. 21 and 22 show how the data on the proportions of the phases present at the various temperatures are used to plot the full constitution history for each of the compositions. This is the type of chart already used so effectively by Sauveur.

A horizontal across the chart at any temperature level shows the percentage constitution of the whole laid off by the curves, which are drawn in a characteristic manner, demanded by the particular composition. The solid equilibrium is made up by the assembling of all these constitution charts. The particular advantage of these individual charts is that they permit the location of the critical points by extrapolation with greater accuracy than would the mere knowledge that it lies somewhere

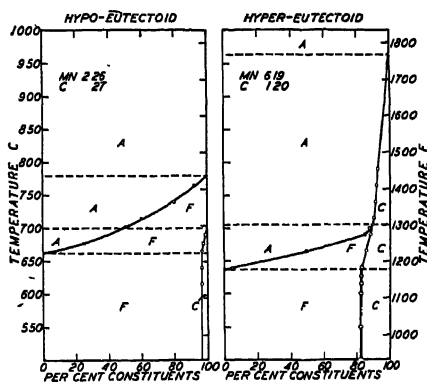


FIG. 21.

FIG. 22.

FIG. 21.—CONSTITUTION CHART FOR A TYPICAL HYPOEUTECTOID ALLOY.

FIG. 22.—CONSTITUTION CHART FOR A TYPICAL HYPEREUTECTOID ALLOY.

between two limiting temperatures. The examples chosen are representative of the two classes of alloys in the series, hypoeutectoid and hypereutectoid. The dashed horizontal lines in the charts mark the critical temperatures.

EXTRA-EQUILIBRIUM CONSTITUTION

From an inspection of the time-at-temperature requirements (Fig. 17) for equilibrium as well as from the evidence of many practical experiences, it is clear that, in use, the steels herein described will in general not exist

¹² V. N. Krivobok: A Study of the Constitution of High-manganese Steels. *Trans. Amer. Soc. Steel Treat.* (1929) 15, 893.

FIG. 18.—TYPICAL PHOTOMICROGRAPH OF FERRITE IN EQUILIBRIUM WITH AUSTENITE (NOW TRANSFORMED) IN AN ALLOY CONTAINING APPROXIMATELY 1.0 PER CENT MANGANESE AND 0.24 PER CENT CARBON. 1 PER CENT NITAL ETCH. $\times 1200$.

FIG. 19.—TYPICAL PHOTOMICROGRAPH OF CARBIDE IN EQUILIBRIUM WITH AUSTENITE IN AN ALLOY CONTAINING APPROXIMATELY 13.0 PER CENT MANGANESE AND 1.20 PER CENT CARBON. 1 PER CENT NITAL ETCH. $\times 1200$.

FIG. 20.—TYPICAL PHOTOMICROGRAPH OF AUSTENITE (NOW PARTLY TRANSFORMED) IN EQUILIBRIUM WITH FERRITE AND CARBIDE IN AN ALLOY CONTAINING APPROXIMATELY 6.2 PER CENT MANGANESE AND 1.20 PER CENT CARBON. 1 PER CENT NITAL ETCH. $\times 1200$.

in the state of true equilibrium, but in some state of permanent persistence wherein the tendency to further readjustment is unable to overcome the inertness of the metal toward any change. Any consideration of the system as a whole out of equilibrium must refer to some specific series of reproducible treatments constant for all. Such conditions might be "water quenched" or "air cooled," for example. These two particular conditions have been studied for the entire series and the results have been plotted in Figs. 23 and 24. The particular constituents or aggregates that result from the specified treatments named are plotted on the composition coordinates. To some extent with the air-cooled specimens, and to a greater degree in the case of water-quenched specimens, the microstructure is not uniform across the entire cross-section of the $\frac{1}{2}$ -in.

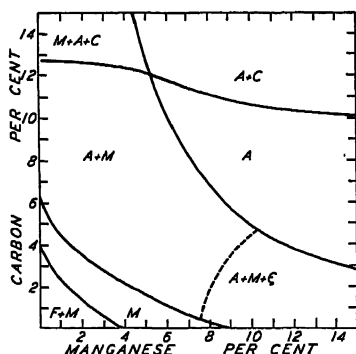


FIG. 23.

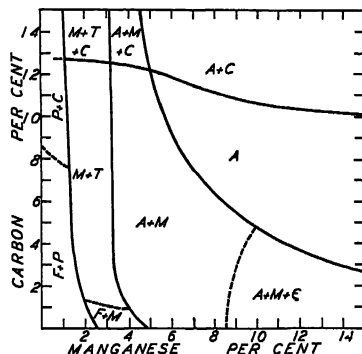


FIG. 24.

FIG. 23.—EXTRA-EQUILIBRIUM CONSTITUTION CHART FOR CONDITION RESULTING FROM WATER QUENCH FROM 950° C. (1740° F.).

FIG. 24.—EXTRA-EQUILIBRIUM CONSTITUTION CHART FOR CONDITION RESULTING FROM FREE AIR COOL FROM 950° C. (1740° F.).

square bars employed. The structure designated on the chart refers to that found in a zone halfway between surface and center in the $\frac{1}{2}$ -in. square cross-section.

These charts are introduced here in the hope of providing a more acceptable substitute for the Guillet diagrams, which, unfortunately, have been reproduced from time to time in various textbooks and reference works. These diagrams of Guillet do not appear to refer to any specific treatment other than air cooling, and it is doubtful whether any single treatment would result in the structures designated for the compositions.

A refrigeration to liquid air temperature results in the formation of martensite in some alloys which otherwise would remain wholly austenitic at room temperature. Similarly, a large family of alloys that undergo a slight partial decomposition of austenite by quenching or slow cooling, or which retain considerable austenite after quenching, are affected by such

refrigeration in a manner to transform some of their austenite to martensite. The alloys here described have been subjected to liquid air cooling, and to illustrate the effect of this treatment Fig. 25 shows the shift in limiting composition for the wholly austenitic alloys brought about by the liquid air refrigeration. Very similar pairs of curves could also be drawn nearer the pure iron corner of the diagram, illustrating the shift of the half-austenitic alloys. For these curves the X-ray crystallograms were employed in conjunction with the microscopic observations. Where the austenite had transformed to an easily recognizable martensite, the microscope was useful, but such cases were rare; the X-ray analysis is wholly without ambiguity although it does not possess great inherent precision. So far as is known, such charts could not be made at the present time except by the use of X-rays.

SUMMARY

A series of iron-carbon-manganese alloys of selected composition, up to 1.5 per cent carbon and 15 per cent manganese, has been studied as to constitution after equilibrium had been established at a variety of temperatures. The data from this investigation of alloys of commercial purity have been assembled in the form of a solid three-component diagram, sections of which are herein presented. Care was exercised to insure equilibrium, which is in general realized only after long periods of time at temperature. The unusually long intervals of heating employed in this study in order to approach equilibrium must clearly produce results at variance with many of those heretofore reported. It is believed that all such discrepancies have to do with the failure of ordinary intervals of time to bring about equilibrium conditions.

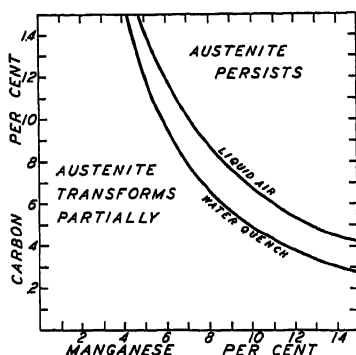


FIG. 25.—LIMITING COMPOSITIONS OF ALLOYS WHICH WILL JUST REMAIN WHOLLY AUSTENITIC WITH WATER QUENCH AND WITH LIQUID AIR TREATMENT.

ACKNOWLEDGMENTS

The alloys employed in this study were obtained through the courtesy of the Illinois Steel Co., South Chicago, Ill., and the authors wish to express their great indebtedness to Mr. Charles L. Kinney, Jr., director of the Physical Laboratory at that plant, for the skillful preparation of these materials according to fine steel practice. To the authors' associates who have assisted in this work thanks are likewise due, particularly to Dr. R. H. Aborn and Mr. J. J. B. Rutherford, who prepared X-ray crystallograms of the specimens.

DISCUSSION

(F. N. Speller *presiding*)

F. T. SISCO AND J. S. MARSH, New York, N. Y. (written discussion).—Because of the prime importance of the iron-carbon-manganese system, metallurgy is deeply indebted to Messrs. Bain, Davenport and Waring for their presentation of so complete a study of the system. One aspect of the study is, in our opinion, of sufficient general importance to stress unstintingly, for cognizance of it must come sooner or later by all investigators of metallic systems: that is, the authors' broad use of methods insuring substantial equilibrium for determination of critical points. More and more evidence is accumulating, which indicates that thermal analysis is frequently unreliable, especially when low-temperature transformations are involved.

We feel sure that the diagrams presented by the authors will become known as the first that are capable of explaining phenomena encountered in manganese steels; in other words, that the diagrams are the first elucidation of the iron-carbon-manganese system which approaches satisfaction.

Because these diagrams undoubtedly will serve as a starting point for future investigations, we propose to examine them from the standpoint of high-purity alloys, despite the fact that the authors expressly state that their diagrams are for alloys of *commercial* purity. By doing so, we hope that further interest may be stimulated in the iron-carbon-manganese system, which thus far has defied complete analysis. Further advances could follow rapidly, since Messrs. Bain, Davenport and Waring have laid such considerable portions of the foundation.

To deal in generalities for a moment, we believe that the iron-carbon-manganese system provides an excellent starting point for investigation of carbides in ferrous alloys, for an understanding of carbide behavior in alloy steels is of sufficient importance to warrant complete investigation. It would, for example, be of considerable interest to know the actual manner of interaction of iron, carbon and manganese atoms in the carbide. This problem becomes of considerable importance when carbon and manganese concentrations are extended beyond those employed by the authors.

The status of epsilon phase remains interesting. The work of Scott and Walters seems to indicate that pressure plays an important role. If so, it is quite possible that epsilon phase is a stable phase at high pressures. Since this phase is closest packed of the iron-manganese system phases, and since there is a known tendency to favor the closest packed phase at elevated pressures, we suggest that investigations of the effect of pressure might be fruitful.

To return to the paper proper, we should like to direct attention to Figs. 4 to 8. Even though the boundaries of the F fields of these sections probably were not determined experimentally, and are therefore somewhat immune from questioning, we feel sure that the authors will agree that the junctions of the F and $F + A + C$ fields should be a single point to be in accordance with the phase rule. (The point being a section of the line of the solid diagram.)

Another point to which we should like to direct attention is the appearance of the isothermal sections which may be derived from the authors' sections. In isothermal sections of three-component diagrams, we would expect three-phase areas to be triangular.¹³ Isothermal sections of the three-phase regions derived from the authors,

¹³ See, for example, E. Scheil: *Mitt. a. d. Forsch. Inst. d. Ver. Stahlwerke A.-G., Dortmund* (1927) 1, 3. In substance, Scheil says "Three-phase regions are separated from two-phase regions by ruled surfaces." (In a footnote he defines a "ruled surface," as understood in his paper, as a surface generated by a straight

diagrams are not triangular. We believe that this point should be clarified, for, assuming the necessity of the aforementioned triangles, deviations of the boundaries shown by the authors from the equilibrium boundaries of the iron-carbon-manganese diagram are implied.

Finally, and incidentally also, we should like to augment the emphasis laid upon the unsatisfactory state of knowledge of the iron-manganese system by the authors. Even though this diagram serves only to establish the origin of lines determined by the authors, we suspect that it may prove to be much more complicated than is indicated by Fig. 9, and hope, therefore, that additional work will be forthcoming.

Despite the contribution of magnitude of the authors, much remains undone on the whole system; we hope that they will continue this important work.

H. SCOTT, East Pittsburgh, Pa. (written discussion).—The authors of this paper were obliged to adopt some definite viewpoint on equilibrium in the solid state before they could present their data consistently. One viewpoint is that the difference in temperature between the start of a transformation on heating and that on cooling will vanish with an infinitely slow rate of temperature change. That apparently is the view of the authors and is one having the authority of tradition. It is well to consider the consequence of this view more fully than is done in the paper, however; otherwise the diagrams presented may appear to controvert experience glaringly.

In the iron-carbon diagram the difference between the Ac and Ar transformations is comparatively small. Consequently it is difficult to establish whether or not the difference will vanish as the rate of temperature change diminishes. The Ac points respond less to rate of temperature change than do the Ar points, so more weight has been given to the Ac points than to the Ar in constructing "equilibrium" diagrams. That also appears to be the practice of the authors.

A weighted mean for the "equilibrium" transformations in iron-carbon alloys does not give a diagram differing much from that for Ac points with usual rates of heating and for that reason has been acceptable in practice. In the iron-manganese system, however, the separation between Ac₃ and Ar₃ becomes very large, 200° C. or more, at high manganese contents. Hence the maintenance of the equilibrium concept becomes much more difficult in that field. Evidence was presented last year by Walters and Gensamer¹⁴ and by the writer¹⁵ showing that the temperature at which the A₃ transformations start, though widely separated, are influenced very little by rate of temperature change. To construct an "equilibrium" diagram, therefore, one must either take values that correspond closely to those observed on heating only or else take a weighted mean which of course will not agree acceptably with observations taken either on heating or cooling. The authors apparently have chosen the former and preferable alternative, so their results, Figs. 1 to 15, give no information on the location of the transformations on cooling, although that is not stated in the text.

The difficulties of harmonizing the concept of equilibrium in the solid state with experiment suggest that possibly more can be gained by dropping that concept than

line moving along two curves as directors, while parallel to horizontal plane.) "The directors of these ruled surfaces are the edges of the adjoining one-phase regions. Thus the three-phase regions are trilateral. They degenerate to a straight line when they meet a binary system (plane) or a quasi-binary section. They remain triangular, however, when meeting a four-phase plane, and cover either the whole or a part of the four-phase plane." It follows that isothermal sections of three-phase regions are triangular.

¹⁴ Reference of footnote 4.

¹⁵ Reference of footnote 7.

by perpetuating it. Perhaps we have lost sight of a fundamental fact by adhering too closely to this analogy taken from liquid-solid reactions. Is it not probable that a certain minimum potential represented by the temperature difference between the A_c and A_r points is necessary to start a change in space lattice and that this potential is higher the lower the temperature?

In regard to the experimental findings, the chart showing the boundary of the gamma field at normal and liquid air temperatures, Fig. 25, is open to question. The curves in the upper left portion are not compatible with a simple general relation between the content of nickel, manganese and carbon and the location of A_r , which I have advanced.

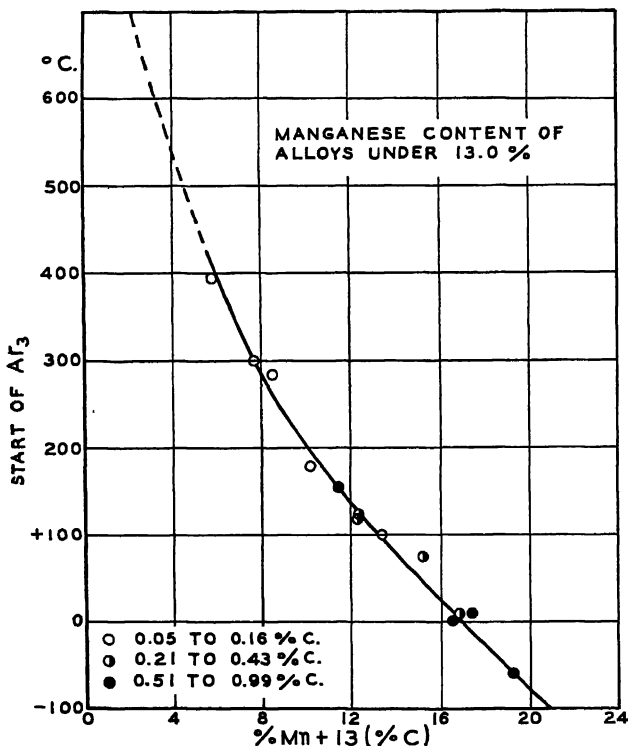


FIG. A

FIG. 26.— A_{r3} IN Fe-Mn-C ALLOYS WHEN ALL THE CARBON IS RETAINED IN SOLID SOLUTION.

It was shown that for a fairly wide range of compositions the location of A_{r3} is constant so long as the sum of the contents of those elements multiplied by certain constants remains unchanged. If that is true the boundary lines of Fig. 25 should be straight rather than curved asymptotic to the axes.

The equivalence of manganese and carbon in lowering A_{r3} for high contents of carbon has recently been evaluated accurately, with the results shown in Fig. 26. Here the temperature at which A_{r3} starts is plotted against the manganese content plus 13 times the carbon content. A_{r3} was determined in alloys differing widely in carbon content and so cooled as to retain all the carbon in solid solution. Since the observed points fall on or very close to the curve and represent carbon contents between

0.05 and 1.0 per cent, the equivalent manganese content at a particular temperature gives the gamma iron boundary compositions for that temperature. We may, for example, express the boundary composition for which A_3 starts at 0°C. by the relation:

$$\text{Percentage of Mn} + 13.0 (\text{percentage of C}) = 17.0$$

For comparison with Fig. 25, the manganese contents are plotted against the carbon contents satisfying the foregoing relation in Fig. 27. The new curve agrees substantially with the authors' curve in the region 6 to 13 per cent Mn. At higher manganese contents their curve is undoubtedly more nearly correct for manganese additions then become increasingly less effective in lowering A_3 . At lower manganese contents (higher carbon), however, there is a wide divergence. The straight

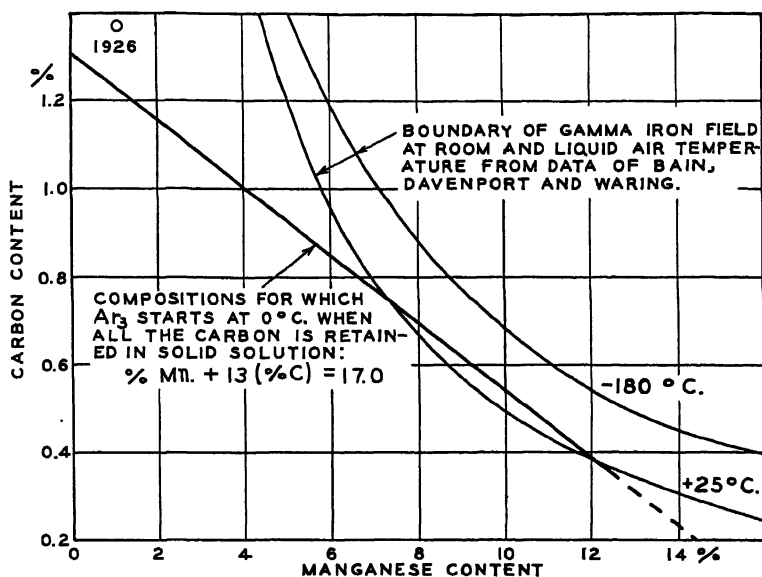


FIG. 27.—MANGANESE CONTENT PLOTTED AGAINST CARBON CONTENT, SATISFYING RELATION IN FIG. 26.

line is an extrapolation for manganese contents under 4.5 per cent, but a check in this region is furnished by an observation on a 1.0 per cent Mn, 1.37 per cent C steel published by the writer in 1926. This steel was entirely austenitic as quenched, but transformed on cooling below room temperature.

An obvious explanation of the discrepancy is that the authors quenched their hypereutectoid alloys from just above the A_{c1} transformation and consequently failed to bring all the carbon into solid solution. If this is not the case there may have been a considerable separation of carbide during the initial stage of the quench, which would have just the same effect as failure to obtain complete solid solution. Carbide separation is likely to occur in the interior of the specimen, but not near the edges. This was shown by the writer in 1923. It is probable, therefore, that a re-examination of the specimens or a more complete statement of experimental details will bring the apparent contradictions into harmony.

E. C. BAIN, E. S. DAVENPORT AND W. S. N. WARING (written discussion).—We are indebted to Messrs. Sisco and Marsh for their painstaking and scholarly discussion of this paper from the viewpoint of physical chemistry, and particularly for calling attention to an error in principle in Figs. 3 to 8. They are, of course, justified in wish-

ing to see even the "dotted" portion of the diagrams drawn in accord with the demands of the phase rule. The narrow ferrite zone at the left of these sections should meet the three-phase zone only at a point. We are pleased that Messrs. Sisco and Marsh attach much the same significance to methods of study which involve a positive approach to equilibrium conditions at constant temperature that we do. Such methods are in contrast to all sorts of continuous heating and cooling cycles, which, in our opinion, must of necessity give evidence of transformations occurring at temperatures displaced from the true equilibrium temperatures. We have had the pleasure of informal communications with Messrs. Sisco and Marsh in the course of which the matter of our isothermal sections of this three-component system were discussed, although they were

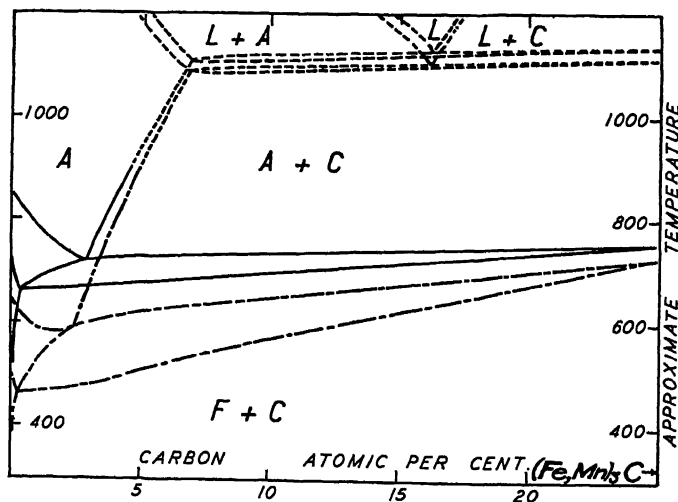


FIG. 28.—CHART SHOWING SCHEMATICALLY PHASE BOUNDARIES IN TWO UNIFORM MANGANESE SECTIONS OF SOLID THREE-COMPONENT DIAGRAM. SOLID LINE, 4 PER CENT MN; DOT-DASH LINE, 13 PER CENT MN.

not included in the paper. In view of the very appropriate material adduced in their discussion, it seems advisable to append a few more words on the behaviors of high-alloy systems which will undoubtedly have a bearing on any equilibrium studies of this character.

Fig. 28 sets forth schematically the probable extension of two uniform manganese sections of the system (approximately 4.0 per cent and 13.0 per cent Mn), as far as the pure carbide phase, which we believe is a single-phase constituent of the cementite crystal form, but having a wide range of composition represented by $(\text{Fe}, \text{Mn})_3\text{C}$. It appears reasonable to expect that this phase is represented by a vertical wall in the solid diagram stretching from Fe_3C on the Fe-C side, toward, but not reaching, Mn_3C on the Mn-C side of the diagram. The three-phase, lenticular shaped zone through the diagram is fairly flat, so that its boundaries are not discovered accurately without the highest precision of measurement. At any rate, this zone makes contact with the carbide wall in a line which slopes downward from the iron-rich to the manganese-rich end.

This being the situation at equilibrium, the isothermal sections at two temperatures, for example 685° and 710°C ., should appear about as in the schematic diagrams of Figs. 29 and 30.

Actually, however, our results when plotted in isothermal sections show a divergence of the boundaries of the three-phase zone as carbon increases, instead of the

convergence demanded by the theory of heterogeneous equilibrium in three-component systems. Clearly then, absolute equilibrium at a precise temperature level was not reached; and in our opinion it may be inherently impossible to achieve equilibrium.

A considerable variety of compositions at a temperature within the three-phase zone should contain a carbide phase of constant composition, but in our experience the manganese-rich alloys seem always to produce a manganese-rich carbide. It is suggested by way of explanation that the first carbide to form is not of the correct final composition. This is the usual state of affairs in the formation of almost any new

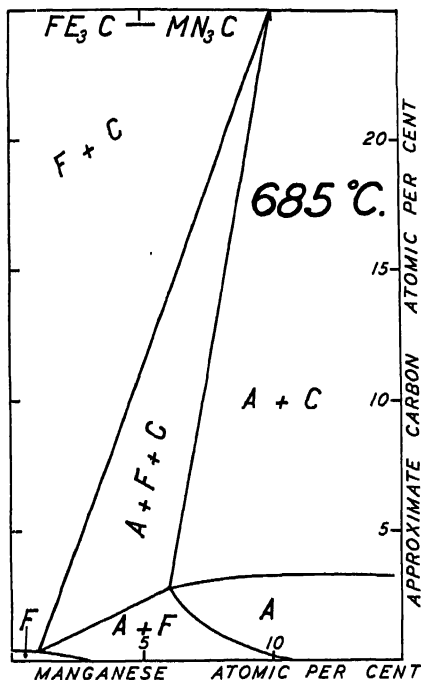


FIG. 29.

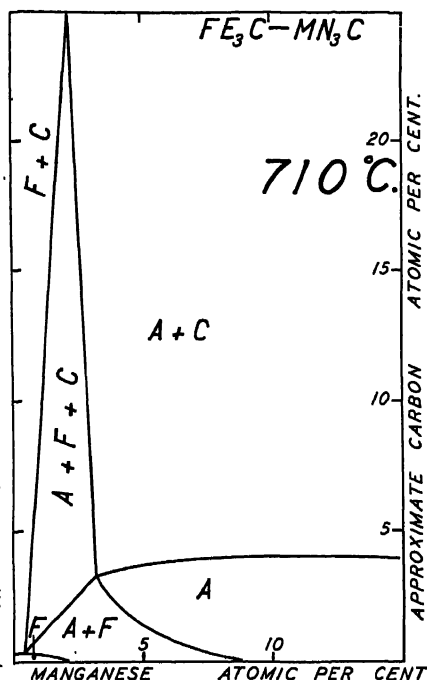


FIG. 30.

FIG. 29.—SCHEMATIC ISOTHERMAL SECTION AT ABOUT 685° C. OF PORTION OF SOLID THREE-COMPONENT DIAGRAM.

FIG. 30.—SCHEMATIC ISOTHERMAL SECTION AT ABOUT 710° C. OF PORTION OF SOLID THREE-COMPONENT DIAGRAM.

phase which may have a range of compositions. But the carbide crystal is an atomic edifice of such rigidity that diffusion is impossible and hence the succeeding deposited carbide has an ever-changing composition. This circumstance would affect the composition of the solid solution phases, austenite and ferrite, and ferrite would appear where only austenite should have accompanied the carbide at equilibrium on the one hand, and austenite exists where only ferrite should have been in equilibrium with carbide on the other.

If longer times will actually accomplish composition adjustment in carbide particles, then such times must exceed thousands of hours at temperatures below about 700° C. We should not be surprised to find that this aspect of final equilibrium would not be realized in any finite time; since the "driving force," so far as the three-phase region is concerned, would appear to be so very small and the "quasi-frictional" resistance so very great.

In cases of this kind one may either speculate on what conditions would be found at ultimate equilibrium or content himself with whatever degree of approach to equilibrium can actually be brought about. And this statement, in turn, so far as the carbide phase is concerned, emphasizes the validity of Mr. Scott's inquiry.

Mr. Scott has so extensively investigated the alloys of iron and manganese that any comments of his on the observed behaviors of the alloys are always worthy of the most serious consideration. We believe that Mr. Scott has not rightly understood our method of study when he says that more weight has been attached to the Ac points than to the Ar points in determining the diagrams. In our equilibrium investigations we have never attached any significance to Ar points, and only rarely have we made any heating curves, and to these we have attached only preliminary exploratory significance. It is our opinion that the ordinary continuous heating and cooling curves have little to do with equilibrium determinations in high-alloy steels.

When, for example, Mr. Scott refers to his work and that of Walters and Gensamer as indicating that the rate of cooling has little influence upon the locations of A_s, we assume that he implies that rates of cooling, even very different from those employed by these investigators, would likewise have little or no influence. Now, to cite an example, if these investigators had cooled an alloy containing about 9.0 per cent Mn and about 1.1 per cent C from about 570° to about 540° C. over a period of time amounting to about 500 hr. (an unreasonably slow rate, to be sure), they would have secured complete transformation of the alloy to ferrite and carbide in substantial accord with the equilibrium diagram, as set forth in our paper. The degree of undercooling here is probably a function of the rate of cooling, as usual, except that for the alloys rich in manganese the transformation does not appear to take place in any finite time unless provision is made for maintaining the austenitic steel at a temperature just below the lower A₁ point for hundreds of hours.

Mr. Scott calls attention to the advantage of having at hand a diagram showing the temperatures of transformation as they actually occur in the system for some certain fixed rate of cooling used throughout, and we likewise appreciate the desirability of such a chart. An equally interesting companion chart would be one showing the temperatures of actual transformation during heating at some certain specified rate. However, that information was not secured nor intended to be part of our paper, for our work relates only to the conditions which we believe approached equilibrium. Although clearly it is a matter of opinion, we are inclined to the belief that the concept of equilibrium, so widely accepted at the present time, has a great deal of merit even in respect to practical utility. It is entirely probable that a "certain minimum potential represented by the temperature difference between" the Ae (not Ac) "and Ar points is necessary to start a change in space lattice and that this potential is higher the lower the temperature." However, when one maintains the alloy at a constant temperature over periods of thousands of hours this temperature difference in cases of solid solution amounts probably only to a few degrees.

Turning to Mr. Scott's discussion of experimental findings, for which he has kindly introduced the chart showing the boundary of the gamma field, we believe, too, that some discrepancy would result from the circumstance pointed out by Scott that our materials for this particular extra-equilibrium study were not quenched so as to have all carbon dissolved. However, it must be quite apparent that Scott's straight-line theory of equivalency of manganese and carbon cannot be broadly correct when he himself finds a departure at the low-carbon high-manganese end of the line and when it is likewise remembered that no amount of carbon in a steel containing little or no manganese can provide for its being brought to room temperature in the wholly austenitic condition. One must conclude therefore that the apparent equivalency extends over a limited range of manganese and carbon. With these modifications one is forced to plot a curve differing not very greatly from that shown in our chart.

Effect of Vanadium in High-speed Steel

By A. B. KINZEL* AND C. O. BURGESS,† NEW YORK, N. Y.

(New York Meeting, February, 1932)

ALTHOUGH vanadium is an important constituent of almost every brand of high-speed steel manufactured today, little is known as to its role in this series of alloys. The now standard 18 per cent tungsten and 4 per cent chromium constituents were the result of developments and improvements before 1903. In that year, vanadium was added to the steel by Dr. J. A. Mathews. This proved to be an outstanding contribution, so that the standard high-speed steel of today is generally referred to as the 18-4-1 type—18 per cent W, 4 per cent Cr and 1 per cent V. Various modifications have been attempted since then, but with the exception of the introduction of cobalt, no striking improvements have occurred. Vanadium has been increased to 2 per cent in many of the common brands, and at least one brand contains 5 per cent V in addition to the usual tungsten and chromium. The carbon has been gradually increased so that it is not uncommon to find 0.80 per cent in the standard grade, although the carbon in the 5 per cent vanadium steel mentioned above is approximately 1 per cent, and even 1.2 per cent has been made experimentally.

The role of vanadium has never been well understood, and although vanadium has been increased to 2.5 and even 5 per cent in certain high speed steels, it has not been generally established that the higher vanadium contents result in superior cutting properties. However, in all of the investigations, of which the writers are aware, the interrelation of the vanadium and carbon contents was not considered as a prime factor. The carbon content was held at 1.2 per cent or less—generally at the usual 0.65 to 0.75 per cent.

THEORETICAL ASPECTS

Although the role of vanadium is not understood, there are theoretical considerations which indicate definite reasons for the improved cutting efficiency due to vanadium. Refinement of the secondary grain is one distinct possibility. The well-known action of vanadium in limiting grain size might well be expected to operate in high-speed steels, and even though its action were not evident in the parent austenite grain.

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it might well function in producing minimum grain size in the ferritic mass. Vanadium is also a powerful carbide former; *i. e.*, the carbide is extremely stable and has a high free energy. It is probable that vanadium carbides are more soluble in ferrite at high temperatures than the tungsten or chromium carbides. If complex carbides were considered, it is possible that vanadium in these carbides would render them more soluble in the ferrite. With a relatively wide variation in solubility of these carbides in the ferrite at high and low temperatures, precipitation of a large number of very fine carbides in the matrix would be expected. These carbides might well improve the cutting efficiency without having apparent effects on the physical properties as usually measured. Moreover, increased solubility in the ferrite would tend to inhibit rejection of carbides to the grain boundaries during the transformation. Thus the possibility of dissolving all the carbides in the austenite on reheating for forging is greatly enhanced, while grain boundary segregation is inhibited and the forgeability of the alloy consequently improved. Furthermore, as vanadium carbide is very stable, it should reduce surface decarburization and thus make for higher cutting efficiency under conditions in which this plays a part.

Vanadium is a well-known ferrite stabilizer, and increased vanadium in a steel already containing 18 per cent W and 4 per cent Cr, with the usual carbon content, restricts the gamma loop so that at optimum hardening temperatures appreciable quantities of delta iron are present unless the carbon is sufficiently high. In our opinion this delta iron formation is the reason for the common belief that vanadium in excess of 2.5 per cent is not beneficial when added to 18 per cent W, 4 per cent Cr high-speed steel of the usual carbon content.

VANADIUM IN STEELS OF USUAL CARBON CONTENT

In order to study the effect of vanadium, a series of heats was made with the usual carbon, tungsten and chromium contents and increasing percentage of vanadium. The analysis of these heats is listed in Table 1. The heats were made in the 6-lb. induction furnace, cast into ingots

TABLE 1.—*Analysis of High-vanadium Steels with Usual Carbon Content*

Heat No.	Composition, Per Cent					
	C	V	W	Cr	Mn	Si
1	0.65	1.22	17.29	4.02	0.52	0.61
2	0.80	2.30	17.09	4.05	0.55	0.70
3	0.64	3.57	16.89	3.95	0.61	0.72
4	0.70	4.55	17.21	3.91	0.51	0.62
5	0.72	7.29	16.94	3.76	0.53	0.80
6	0.70	9.77	16.16	3.92	0.61	1.10

and forged without difficulty at the usual temperatures. It is particularly interesting that the steels containing more than 3.5 per cent vanadium forged like straight carbon steels rather than like high-speed steels. The steels were cooled as $\frac{5}{8}$ to $\frac{3}{4}$ -in. squares in still air, and hardness readings were taken. The bars containing up to 2.30 per cent vanadium showed a Rockwell C hardness of 59, whereas the bars containing 3.5 to 9.77 per cent vanadium showed a hardness of 22 to 31. All bars were then quenched from 1285° C., and the Rockwell C hardness was measured. The results are shown in Fig. 1, in which vanadium content is plotted against hardness. The sharp drop in the hardness curve with small change in vanadium composition undoubtedly is indicative of

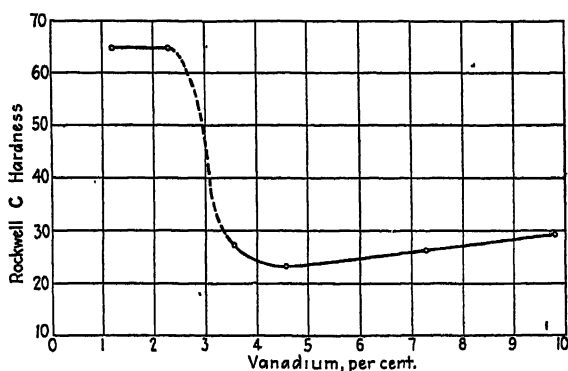


FIG. 1.—ROCKWELL C HARDNESS AGAINST VANADIUM CONTENT OF OTHERWISE STANDARD HIGH-SPEED STEEL.

the border line at which delta iron largely suppresses the formation of gamma iron in the steels at high temperatures. When this occurs, the formation of a hard martensitic groundmass is inhibited, and a decided drop in hardness results. The slight increase in hardness of the steels containing from 4.5 to 9.77 per cent vanadium is believed to be due to the precipitation hardening of the ferrite by the vanadium carbides.

A study of the microstructure of these steels shows that with vanadium at 3.57 per cent or over (the compositions corresponding to the lower branch of the curve, Fig. 1), free carbides are reduced, and the groundmass does not show martensitic markings.

INTERRELATION OF VANADIUM AND CARBON

In the belief that the effect of vanadium in higher percentages was due to the delta iron formation at the higher temperatures, carbon was added in order to offset the vanadium effect, the carbon being an austenite stabilizer at these temperatures. Several heats were made with carbon running from 1.20 to 2.20 per cent and vanadium from 3 to 7 per cent. The analysis of these is shown in Table 2. Ingots 12, 14, 15 and 16

broke up during forging. Ingot 12 cracked badly. Ingot 15 cracked after some reduction, and ingots 14 and 16 cracked only after appreciable reduction, indicating that the analysis of these ingots is just beyond the limit of forgeability. No difficulty in forging was experienced with

TABLE 2.—*Analysis of High-vanadium and High-carbon Steels*

Heat No.	Composition, Per Cent					
	C	V	W	Cr	Mn	S
11	1.20	3.77	17.42	3.80	0.29	0.36
12	2.16	3.36	16.36	3.78		
13	1.52	5.05	17.02	3.76		
14	1.94	4.82	18.44	4.00 ^a		
15	2.26	4.99	16.54	3.74		
16	1.81	7.34	16.87	3.97		

^a Approximate.

the other two ingots, 11 and 13, which gave Rockwell C values of 62 as forged. Torch specimens of these heats were then prepared by holding one end of a $\frac{1}{4}$ -in. square in cold water and melting the other end with an oxyacetylene torch. This produced a temperature gradient covering the entire temperature range of interest. Quenching the specimens under these conditions retains in essence the structure corresponding to the various temperatures. Hardness tests along the specimen showed maximum hardness of 68 Rockwell very close to the fused material. Drawing the specimens at 560° C. did not lower the hardness in the zone quenched from a high temperature, but did lower it in the parts of the specimen which were at lower temperature before quenching.

In order to further investigate quenching temperatures, specimens from heats 11 and 13 were oil-quenched from 1000°, 1100°, 1200° and

TABLE 3.—*Quenching Temperatures*

Heat No.	Rockwell Hardness C, When Oil-quenched			
	From 1000° C.	From 1100° C.	From 1200° C.	From 1285° C.
11	58	63	66	67.5
13	60	63	65	67.5

1285° C. The Rockwell hardnesses obtained on these quenched specimens are shown in Table 3. This indicates that in this steel, as in the usual high-speed steels, the optimum hardening temperature is the optimum practicable temperature, so 1285° C. was used for the oil-

quenching of tool bits for lathe tests. The lathe tests on material undrawn showed the residual stresses to be too high for practical operation. Accordingly the specimens were tempered at 560° C., and again lathe tested. It was particularly noteworthy that this tempering operation did not affect the Rockwell hardness. It is also significant that on cutting 0.50 per cent carbon steel of 250 Brinell, no difficulties were experienced with spalling or cracking of the tool, nor were there any indications that the toughness of the material was insufficient. This study of the thermal treatment is necessarily limited in scope. It may be that higher quenching temperature or varying holding time at temperature, as well as higher drawing temperatures and longer drawing times, would result in still better cutting properties.

VANADIUM AND CARBON IN COBALT STEELS

As the superior cutting properties of cobalt high-speed steels are well recognized, the effect of increased vanadium and carbon in these steels was also studied. Heats were made of analysis shown in Table 4.

TABLE 4.—*Analysis of High-vanadium High-carbon Cobalt Steels*

Tool No.	Composition, Per Cent						
	C	V	Co	W	Cr	Mn	Si
21	1.18	4.31	8.76	17.57	3.74	0.22	0.50
22	1.66	6.60	7.40	15.21	3.53		
23	1.36	4.95	2.17	17.03	4.10		
24	1.40	6.22	5.70	17.54	4.10		

Ingots 21, 23 and 24 gave no trouble in forging, but ingot 22 broke during reduction and bars were obtained only with difficulty. On quenching and drawing these steels at the usual temperatures a Rockwell C hardness of 63 resulted. While this was lower than expected, the lathe performance was surprisingly good, so that it appears that carbon and vanadium produce the same phenomena in cobalt high-speed steels as in standard high-speed steels.

LATHE TESTS

It is generally appreciated that the only true test of a lathe tool is a production run under shop conditions. However, much may be learned from controlled lathe tests, particularly when the order of magnitude of the cutting performance is of interest rather than minor variations. There are many ways of lathe testing and the writers chose the simplest one that appears to be reliable; namely, constant cut, feed, and speed on a standard billet with measurement of total length of cut before

regrounding. Tool size was standardized at $\frac{5}{8}$ and $\frac{1}{2}$ in. and the values obtained at $\frac{1}{2}$ in. were corrected to $\frac{5}{8}$ in. on the basis of previous experience with the test conditions and type of steel being cut. Results on a

TABLE 5.—*Results of Lathe Tests*

Test Conditions: 250 Brinell, 0.50 Per Cent C Steel Billet. Speed, 118 to 120 Ft. per Minute; Cut, $\frac{1}{8}$ In.; Feed, 0.040 In.

Tool No.	Tool Type	Length of Chip before Failure, In.	
		First Test	Second Test
1	Standard high-speed steel.....	2298	1680
11	3.8 per cent V, 1.2 per cent C, high-speed steel...	3315	3060
13	5.0 per cent V, 1.5 per cent C, high-speed steel...	4080	4080
21	4.3 per cent V, 1.20 per cent C, 9 per cent Co, high-speed steel.....	6890	
22	6.5 per cent V, 1.7 per cent C, 7.5 per cent Co, high-speed steel.....	5525	
23	5.0 per cent V, 1.35 per cent C, 2 per cent Co, high-speed steel.....	3910	

single billet are shown in Table 5. The order of magnitude of check tests agrees very well and there is a remarkable improvement due to higher vanadium with higher carbon. The same relative performance was found to hold using other test billets.

DISCUSSION OF RESULTS

It is appreciated that the work herein reported is far from being a complete study of the field. The limitations of 6-lb. induction furnace heats are thoroughly understood, but general experience indicates that comparative results on material made in this way may be translated to material made under the usual mill conditions. Owing to the limited data, we hesitate to draw conclusions, but the results are so striking that several generalities are certainly warranted. First, it appears that for each per cent of vanadium, 0.2 per cent of carbon may be added to the 18 per cent W, 4 per cent Cr, 1 per cent V, 0.70 per cent C high-speed steel, without encountering difficulties in forging up to 1.6 per cent C. The upper limit of vanadium and carbon contents has not been well established but remains an interesting field for further study.

In addition to good forgeability, the steels containing the higher amounts of properly proportioned vanadium and carbon show a marked increase in cutting efficiency, with no appreciable falling off in toughness. The same improvements may be obtained by increasing the vanadium and carbon in cobalt high-speed steels. Further work is necessary in order to determine the optimum composition for commercial use, but it is

evident that an improved high-speed steel may be produced by increasing the vanadium and carbon in proper ratio and that the optimum composition is not far from 1.5 per cent C and 5 per cent V. Since the work described was carried out, the writers have learned of the work of Certel and Eilender, which apparently was carried out contemporaneously with the work reported above, and which appears to substantially corroborate many of the findings recorded here.

CONCLUSIONS

1. Vanadium improves the cutting efficiency of the 18 per cent W, 4 per cent Cr high-speed steels if the carbon content is properly controlled.
2. With the standard 18 per cent W, 4 per cent Cr, 1 per cent V, 0.70 per cent C steel as a base, the carbon should be increased approximately 0.2 per cent for each 1 per cent increase in vanadium for optimum forgeability and cutting efficiency.
3. Five per cent V with 1.5 per cent C appears to be a satisfactory composition for 18 per cent W, 4 per cent Cr high-speed steels with good forgeability and improved cutting properties.
4. Vanadium and carbon increased in proper ratio improve the cutting efficiency of cobalt high-speed steel.

ACKNOWLEDGMENT

The writers wish to acknowledge the generous assistance of their colleagues at the Union Carbide and Carbon Research Laboratories, particularly Mr. R. C. Day's supervision of the cutting tests and Mr. J. R. Vilella's micrographic work. They also wish to thank Dr. J. A. Mathews for critical discussion of the results.

DISCUSSION

(*F. N. Speller presiding*)

F. B. LOUNSBERRY, Dunkirk, N. Y. (written discussion).—The authors' results confirm and complete the various isolated experiments of many investigators. As far back as 1922, we did considerable experimenting with different vanadium contents in regular 18-4-1 high-speed steel maintaining the carbon content approximately 0.70 per cent. It is interesting to note that on steel M-539-A (chemical analysis: carbon, 0.73 per cent; chromium, 5.04; tungsten, 16.36; vanadium, 3.48) we make the following comments:

- As rolled, Brinell hardness 241
- Annealed, Brinell hardness 192
- Oil quenched 2350° F., draw, 500° F., Brinell hardness 364
- 900° F., Brinell hardness 346
- 1100° F., Brinell hardness 364¹

Even by quenching into water from 1550° to 1700° F., this steel would not harden. This clearly shows the effect of vanadium on regular high-speed with 0.70 C in restricting hardening and confirms the authors' results as shown in Fig. 1. This effect of vana-

dium in stabilizing ferrite and restricting gamma iron formation has been demonstrated in steels other than high-speed steels.

In 1926 and later the Ludlum Steel Co. manufactured and placed on the market a steel known as High-Van, which had the following composition: carbon, 1.00 per cent; chromium, 4.00; tungsten, 18.00; vanadium, 3.25. This steel conforms almost exactly with the authors' formulas that in 18-4-1 high-speed steel for each increase in carbon above 0.70 per cent of 0.20 per cent C the vanadium content should be increased 1.00 per cent for optimum forgeability and cutting efficiency. This particular high-speed analysis showed exceptional cutting properties in some cases, but was somewhat erratic in results. The principal difficulties encountered, which led to its abandonment, were its manufacturing troubles, poor recoveries and consequent high cost.

Since then other types of high-speed steels with vanadium contents up to 2.00 to 2.50 per cent and carbon up to 0.80 to 0.90 per cent have been successfully produced and marketed, showing exceptional cutting properties for certain applications. In all of these higher vanadium, higher carbon high-speed steels, however, thermal treatment both in forging and rolling, as well as in the final tool hardening, is of utmost importance in order to obtain satisfactory results. It is to be hoped that the authors will continue their investigations further, especially in regard to the thermal treatment.

W. H. KEEN, New York, N. Y. (written discussion).—It is gratifying to see that this paper confirms my work begun in 1915, and culminated in an application for a patent in May, 1924 (U. S. Patent No. 1621886, March 22, 1927).

My work checks quite accurately with that of Kinzel and Burgess in the significant and unusual property brought out in Fig. 1, showing the loss of hardenability when the vanadium content is increased without simultaneously raising the carbon. My tests seemed to indicate that a carbon content of about 0.77 to 0.78 per cent was the danger line below which nonhardening would occur if the vanadium were increased to approximately 2.50 per cent and beyond. I found that 0.80 per cent C and over seemed to be safe in this respect even if the vanadium reached 3.25 per cent or slightly higher. Steels produced commercially under my supervision during the past eight years have been maintained between the limits of 0.90 and 1.10 per cent C. This with approximately 3 per cent V has been found to give a very satisfactory commercial product, decidedly superior to 18-4-1 steels.

Probably 150 to 200 tons of this steel has been produced and marketed in the past few years and on certain difficult jobs has met with considerable favor. Probably one of the best uses for this steel is in the manufacture of form cutters, reamers, and tools where accuracy in maintenance of size is essential. The possibility of consistently getting a Rockwell hardness of C-67 or even C-68 explains this desirable wear-resisting property. Carbides are uniformly distributed and practically never found segregated in longitudinal streaks so often met with in 18-4-1 steel.

On roughing operations it has been my observation as a conservative statement that about 30 per cent improvement can be expected, but on cutting nonferrous metals such as brass and aluminum the improvement is in the ratio of about 4 to 1; a similar performance has been experienced on hard rubber. But it has a further and more important use in machining metals which ordinary tools will not cut; for instance, it makes a good roll turning tool, and will readily machine manganese steel.

One very important precaution is necessary in hardening this steel; *viz.*, careful control of furnace atmosphere. An oxidizing heat will result in partial decarburization to a considerable depth and frequently the carbon will drop to 0.75 or lower, which of course, referring again to Fig. 1, means that cutting performance will not be satisfactory until the tool has been ground away enough to remove entirely this soft skin. Extremely misleading results have been obtained at times and probably will continue to occur under ordinary conditions of hardening.

A hardening heat of 2300° to 2350° F. with a draw to 1050° F. seems to be best for this steel and is in close agreement with recommendations in the paper by Kinzel and Burgess. A higher temperature than 2350° will usually give a burnt structure unless the time factor is extremely small.

The addition of cobalt gives a steel showing still greater improvement, but it is doubtful whether the additional cost is justifiable except for special applications. Prices available in the past have been a limiting factor on the vanadium content. Mill recoveries are lower than on 18-4-1 and in consequence cost of manufacture is considerably enhanced beyond what the calculated composition would seem to indicate.

J. A. MATHEWS, New York, N. Y. (written discussion).—The paper by Messrs. Kinzel and Burgess is interesting although the practical test data in regard to performance leave much to be desired. For years past attempts have been made to increase the vanadium in current high-speed steel analyses and usually with disappointing results because a corresponding increase in carbon has not taken place. We have been working somewhat along the line described in the paper and recently forged some steel very close in analysis to that described. The carbon was 1.40, chromium 4.07, vanadium 5.32 and tungsten 18.69. This steel was heated carefully for forging and given ample time in the heating. The temperature at which the forging was started was 2050° F. The steel worked very hard for the first two heatings but afterwards seemed to forge about in the same way as regular high-speed steel. Preliminary work in hardening and tempering seemed to indicate that the initial hardness is apt to be a little greater than that obtained in 18-4-1 but that after tempering at 1050° to 1100° F. the final hardness seems to be if anything slightly greater with the 18-4-1. Preliminary work would indicate that the heat treatment of the 18-4-5 grade is not as simple as the 18-4-1 grade because the hardening heat required is higher and therefore the timing at heat is more difficult to control.

A. B. KINZEL AND C. O. BURGESS (written discussion).—The data given by Mr. Lounsberry are certainly confirmative of those presented here in the lower vanadium and carbon ranges. Mr. Lounsberry's statement that the nature of vanadium in stabilizing ferrite and restricting gamma iron formation is known in steels other than high-speed steels is true, but we should be particularly careful in applying this rule to the high-speed steels in question. As a matter of fact, we believe that it applies, but this has not been proved by any means, and it is possible that by simple carbide formation and removal of carbon from solid solution some softening effect may be achieved without involving the matter of delta iron. The occasional erratic behavior of the steels manufactured by Mr. Lounsberry may well be due to lack of control of carbon. With only 3 per cent V the carbon content is comparatively critical and it may well be that it was on the low side in these cases.

Mr. Keen's discussion is also corroborative in the lower vanadium and carbon range although he presents no evidence on the 5 per cent V, 1.50 per cent C steel which we have recommended as the optimum analysis. It should be realized that there is a distinct difference between the 5 per cent V and the 3 per cent V steels with corresponding carbon, in that the former steels are so loaded with carbide that a very fine carbide distribution persists at the higher temperatures, resulting in an extremely uniform carbide distribution as well as an evenly graded size distribution of carbide particles; that is, in 5 per cent V steels the carbide particles from the smallest size visible in the microscope at 1000 dia. up to the usual carbide size in fine-grained high-speed steel are present in relatively equivalent quantities. This is not true of the 3 per cent steels, where, in our work, the extremely fine carbides are not evident. The matter of hardening temperature as brought up by Mr. Keen is important, but it is interesting that his work on the lower vanadium steels checks the temperatures which we find to

be optimum. We realize, however, that much remains to be done in this field. The matter of decarburization is a very important one from a practical standpoint. It is our experience that the 5 per cent V steels decarburize much less than the 3 per cent, and it is probable that the uniformity of the excellent mill results that have been reported to us since the presentation of the paper is partly due to this factor.

Information given by Dr. Mathews confirming the forgeability of this grade of steel is appreciated. After the heat treatment, it would be seen from the text that this matter has only been briefly surveyed. However, this survey indicated that there was little difference in the treatment required for the 5 per cent V steels and the standard 18-4-1. As is probably the case with all high-speed steels, the higher the temperature short of burning, the better the result. Thus a slightly lower temperature with a slightly longer time could be used by Dr. Mathews, and while this would affect the cutting qualities to a slight degree, it is believed this effect would be too small to be appreciable.

Resistance of Iron-aluminum Alloys to Oxidation at High Temperatures

By N. A. ZIEGLER,* PITTSBURGH, PA.

(New York Meeting, February, 1932)

A CERTAIN amount of interest has been indicated recently in the resistance to oxidation at high temperatures of iron-aluminum alloys (rich in iron). Hautman¹ published a paper in which some interesting results are given. According to his paper, only alloys containing at least 8 per cent aluminum indicate a marked improvement in their resistance to oxidation. At about this aluminum content, however, alloys become brittle, which considerably reduces their commercial value.

About two years ago the author performed a series of experiments, the results of which are presented here. A series of iron-aluminum-carbon alloys was prepared by melting electrolytic iron, aluminum and high-carbon iron alloy in an induction vacuum furnace.² The list of these alloys is given in Table 1. Each alloy was forged in the ordinary way to

TABLE 1.—*Alloys Used in Experiments*

Alloy No.	Al, Per Cent	C, Per Cent ^a	Alloy No.	Al, Per Cent	C, Per Cent ^a
1	0	0.0009			
2	2.30	0.0015	20	5.20	0.0060
3	1.94	0.0268	21	6.23	0.0457
4	2.28	0.0703	22	6.72	0.0685
5	2.23	0.1775	23	5.74	0.1375
6	1.83	0.2121	24	5.15	0.2386
7	1.54	0.2397	25	5.19	0.3260
10	3.70	0.0029	30	7.95	0.0080
11	3.83	0.0195	31	8.63	0.0530
12	3.45	0.0540	32	6.99	0.0862
13	3.79	0.0752	33	7.55	0.2167
14	3.67	0.1396	34	6.19	0.2999
15	3.73	0.2601	35	7.15	0.3923

^a All carbon determinations were performed by "Yensen" method. [N. A. Ziegler: Recent Developments in Analysis of Carbon in Iron and Iron Alloys. *Trans. Amer. Electrochem. Soc.* (1929) 56, 231.]

* Research Engineer, Westinghouse Electric & Manufacturing Co

¹ *Stahl und Eisen* (Jan. 15, 1931).

² P. H. Brace and N. A. Ziegler: Application of a High-vacuum Induction Furnace to the Study of Gases in Metals. *Proc. Inst. Met. Div., A. I. M. E.* (1928) 544.

1¼-in. octagon bar. Forging was performed without any difficulty, no brittleness being indicated by any one of the bars. Disks ½ in. thick were cut from each bar, and were held for 2 hr. at various constant temperatures from 600° to 1100° C. (at 100° intervals). Heat treatments were performed in a Hoskins furnace in air atmosphere. After every heat treatment samples were removed from the furnace and cooled in air to room temperature. The weight of each sample was determined before heat treatments. After every heat treatment surface scales were removed from samples by grinding and new weight was obtained, thus determining how much material was lost by scaling. Care was taken in grinding to

TABLE 2.—Percentage of Weight Left Unoxidized after Heat Treatments at Different Temperatures

Alloy No.	Al, Per Cent	C, Per Cent	Percentage of Original Weight					
			600° C.	700° C.	800° C.	900° C.	1000° C.	1100° C.
Ni-Cr.....			99.9	99.5	98.9	98.7	98.3	97.5
Ingot iron..		0.0118	99.4	98.1	93.2	88.3	78.3	58.7
0-1	0	0.0009	99.4	97.8	95.0	92.1	84.5	72.9
0-2	2.30	0.0015	99.6	99.2	98.4	97.6	95.6	89.0
0-3	1.94	0.0268	99.5	99.0	98.1	97.9	93.8	91.8
0-4	2.28	0.0703	99.4	98.6	97.9	97.0	92.6	82.4
0-5	2.23	0.1775	99.7	99.2	98.1	97.5	94.4	81.4
0-6	1.83	0.2121	99.6	99.0	98.3	97.5	93.1	81.6
0-7	1.54	0.2397	99.5	99.1	98.4	97.8	93.9	84.0
0-10	3.70	0.0029	99.8	99.2	98.3	97.5	96.0	92.4
0-11	3.83	0.0195	99.6	99.2	98.4	97.6	95.9	89.8
0-12	3.45	0.0540	99.8	99.2	98.4	97.6	96.6	86.4
0-13	3.79	0.0752	99.6	99.2	98.2	97.5	96.7	89.9
0-14	3.67	0.1396	99.6	99.1	98.5	97.9	96.6	86.0
0-15	3.73	0.2601	99.6	99.3	98.5	97.9	96.6	86.6
0-20	5.20	0.0060	99.5	99.0	98.2	98.0	97.0	95.0
0-21	6.23	0.0457	99.8	99.6	99.2	98.6	98.2	96.4
0-22	6.72	0.0685	99.8	99.6	99.1	98.6	98.0	96.2
0-23	5.74	0.1375	99.8	99.3	98.8	98.4	97.3	94.2
0-24	5.15	0.2386	99.9	99.5	98.8	98.2	97.5	91.6
0-25	5.19	0.3260	99.6	99.2	98.8	98.2	97.0	93.4
0-30	7.95	0.0080	99.8	99.4	99.0	98.8	98.7	98.1
0-31	8.63	0.0530	99.5	99.4	99.3	98.6	97.9	97.6
0-32	6.99	0.0862	99.5	99.1	98.6	98.2	97.6	96.5
0-33	7.55	0.2167	99.8	99.3	98.9	98.6	97.9	96.6
0-34	6.19	0.2999	99.5	99.2	98.9	98.2	97.6	96.7
0-35	7.15	0.3928	99.9	99.5	99.2	98.1	97.7	95.1

remove as little nonoxidized (metallic) material as possible. The scaling loss at different temperatures was thus obtained. The resistance to oxidation at different temperatures is given in Table 2. For four typical alloys, it is represented graphically in Fig. 1. A sample of a standard nickel-chromium alloy (80 per cent Ni, 20 per cent Cr)³ and a sample of ingot iron were subjected to the same heat treatments together with these samples. Their oxidation resistances are given in Table 2, and are plotted, for the sake of comparison, on the curves in Fig. 1. Fig. 2 is a space diagram representing the scaling losses of iron-aluminum-carbon alloys, after subjection to 1100° C. in air atmosphere for 2 hr. From the data available, similar diagrams may be constructed for every temperature.

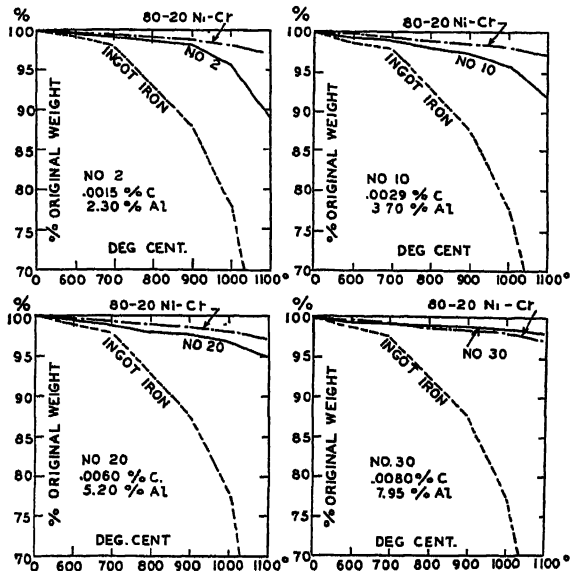


FIG. 1.—RESISTANCE TO OXIDATION OF FOUR TYPICAL ALLOYS.

It may be noticed that even 2 per cent aluminum (Table 2, Fig. 1) alloys show a certain improvement in their oxidation-resisting properties, as compared to ingot iron. At 4 per cent aluminum this improvement becomes appreciable. Alloys with 6 per cent aluminum are only slightly inferior to nickel-chromium alloy, while with 8 per cent aluminum they are just as good and in some cases even superior. Carbon content, on the other hand, has little if any effect on the oxidation-resisting properties of these alloys (Table 2).

It should be remembered that the results described were obtained with laboratory samples, prepared with a great deal of care and precau-

³ This alloy corresponds to nichrome No. 1 and chromel A.

tion. There is no reason, however, why these laboratory results could not be repeated, or at least approximated, on a commercial scale.

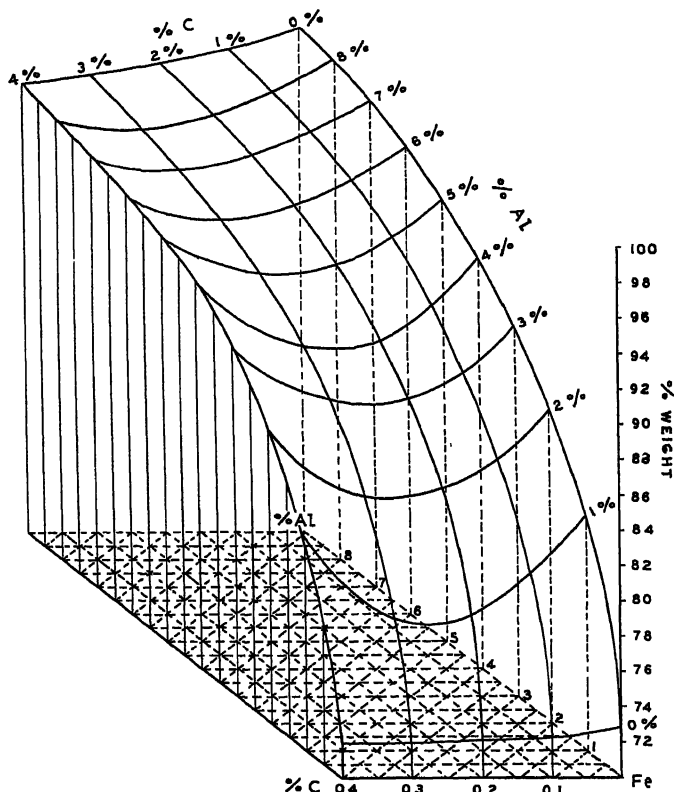


FIG. 2.—SCALING LOSSES OF IRON-ALUMINUM-CARBON ALLOYS AFTER SUBJECTION TO 1100° C. IN AIR FOR TWO HOURS.

ACKNOWLEDGMENTS

The author wishes to acknowledge his indebtedness to Dr. T. D. Yensen for his cooperation in preparing the manuscript and to Mr. Wilson Scott for his help in the experimental part of the work.

DISCUSSION

(F. N. Speller presiding)

F. N. SPELLER, Pittsburgh, Pa. (written discussion).—Mr. Ziegler has shown a marked decrease in rate of oxidation between 0 and 1.5 per cent aluminum content, and a lesser effect in proportion above this percentage of aluminum. It is to be hoped that the work will be continued with a lower percentage of aluminum.

In our work on 18-8 chromium-nickel steels in cooperation with several oil refineries to determine the effect of other elements, it was noticed that 2.75 per cent Al had a

marked effect in decreasing the rate of oxidation. Where the samples with aluminum were inserted into cracking tubes in service very little adherence of coke was found.

F. B. FOLEY, Philadelphia, Pa. (written discussion).—A most interesting point in Mr. Ziegler's paper is that forging of these alloys of iron and aluminum was performed without any difficulty, no brittleness being indicated by any one of the bars, although the aluminum content was as high as 8.63 per cent. The reason for this successful forging may and probably does lie in the fact that the alloys were melted in vacuum. It would be interesting to determine results of forging similar high-aluminum steels melted under normal atmospheric conditions. Alloys of the type of high aluminum content are subject to rapid crystal growth at high temperatures, because of either a very high critical temperature or no critical temperature at all.

N. A. ZIEGLER (written discussion).—The work described here was more or less incidental, being a side issue in connection with magnetic research problems. For this reason it received less attention than probably it should have. It is hoped, however, that the results are sufficiently interesting to stimulate further work on these alloys.

Effect of Heat Treatment on Corrosion Resistance of Stainless Iron

By CLARENCE G. MERRITT,* HARRISON, N. J.

(New York Meeting, February, 1932)

STAINLESS iron, as mild stainless steel is usually called, an alloy ranging from 11.50 to 15.00 per cent chromium with carbon under 0.12 per cent, has been considered to be not appreciably affected in respect to corrosion resistance by heat treatment. This metal, while one of the most widely used of the "straight" chromium stainless alloys, has failed in many applications because of insufficient information regarding heat treatment. These failures have been attributed to many possible causes from an inherent lack of resistance to corrosion and misapplication to mysterious electrolytic effects or comparatively minute non metallic inclusions. Many uses for a steel with such excellent physical properties as are latent in this alloy have been lost on account of corrosion failures which could have been avoided by applying proper heat treatment. The alloy has not received the recognition or attention it should because of the fact that the details of its metallurgical behavior were not thoroughly understood. Response to heat treatment of the steel is well known as regards tensile properties,^{1,2} but its application has been for improvement in tensile characteristics or on account of machining considerations rather than for corrosion prevention. The potential user of this steel has not been clearly advised in papers, either technical or commercial, that have been written about it in the last 10 years or more, of particular features that are of prime importance in developing the excellent properties of this metal. The data to be presented in this paper are concerned mainly with the effect of heat treatment on the corrosion resistance, but a study has also been made of the concurrent microstructural changes and an explanation developed for the phenomena revealed, as well as a correlation to the other physical properties—hardness, tensile characteristics and impact strength.

Stainless steel, largely used for cutlery purposes, an alloy of approximately 13.00 per cent Cr with 0.30 per cent C, must be hardened and the surface prepared by polishing or pickling for best resistance to staining and corrosion.³ Monypenny reports that a loss of hardness is

* Atha Works, Crucible Steel Company of America.

¹ N. L. Mochel: Stainless Iron. *Trans. Amer. Soc. Steel Treat.* (1926).

² O. K. Parmiter: Stainless Steels. *National Metals Handbook* (1930).

³ J. H. G. Monypenny: *Stainless Iron and Steel*. New York, 1931. John Wiley & Sons.

experienced by tempering at 500° to 600° C. (932° to 1112° F.). This is accompanied by a loss in corrosion resistance. While some improvement is noted after tempering at 700° to 750° C. (1292° to 1382° F.), attributed to coalescence of carbides, the applications for this steel have been limited to fields where a certain degree of hardness is desirable. The practice of hardening and polishing is therefore rigidly adhered to in the fabrication of articles from this alloy.

Various problems concerning the corrosion resistance of stainless iron indicated that heat treatment is also an important factor in the use of this alloy. In one particular instance, a sample failed experimentally in a salt-spray test, and was severely rusted and deeply pitted. The chemical analysis, however, was correct. The bottoms of pits were searched microscopically for irregularities of cleanliness or structure with negative results. The material was apparently sound, homogeneous and commercially free from nonmetallic inclusions. A second salt-spray test was made of the same steel re-heat-treated and left in the hardened condition. The specimen, after 100-hr. exposure, showed no rust at all. This seemed reasonable, since it was believed that the increased surface stability was due to the extra amount of chromium dissolved by the treatment. This theory was exploded when a thoroughly annealed piece of the same bar was found to be just as excellent as the hardened specimen. To summarize these findings, quenched steel was resistant, annealed steel was resistant, but the same material hardened and tempered was badly subject to corrosion. There seemed to be an intermediate point between the fully hardened and the fully annealed conditions; in other words, some tempering range where the susceptibility to corrosion was greatly increased. This range was apparently not wide, since various samples almost identical not only in chemical analysis but also in Brinell hardness showed wide variance in degree of attack.

The problem was first studied by testing taper-heated bars and subsequently by the subjection of individually heat-treated pieces to agents of corrosion. Corrosion resistance as referred to in this paper is used to mean commercial satisfaction under service conditions for which the alloy is recommended and comparative attack by salt spray and dilute nitric acid. Very severe conditions—strong hydrochloric acid, for example—produce a violent reaction, so that the effect of the heat treatment is masked by the magnitude of the attack.

MATERIALS AND METHODS

The steels used in this work were all commercial electric furnace products, hot-rolled. Heat-treating and annealing tests were made by laboratory methods with careful control of time and temperature.

Brinell hardness tests were made with a 10-mm. ball and 3000-kg. load. Tensile tests were made on standard 0.505-in. round 2-in. gage

threaded specimens. Impact tests were made on a Charpy machine using 0.394-in. square specimens with a V-notch 0.079 in. deep, giving an area of impact of 0.124 square inches.

Taper-heated tests were made on round bars, one end of each being placed in water while the other end was heated by an acetylene flame to a temperature of approximately 1900° F. A heat gradient was produced in this way which conditioned the bar from its original state through every drawing temperature to the annealed condition.

The heated end was hot enough to produce an air-hardened portion, giving in one test not only descending hardnesses from the original

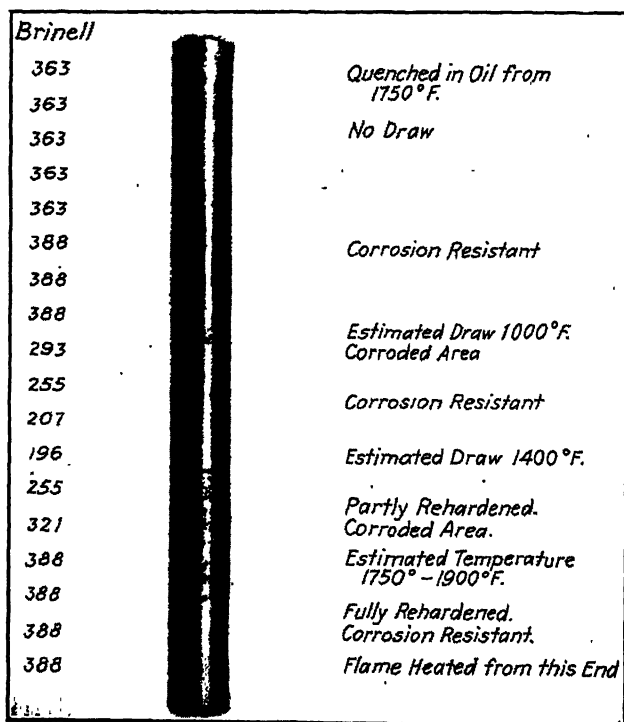


FIG. 1.—TAPER-HEATED TEST. MATERIAL 3637-2.

Quenched all over in oil from 1750° F. Taper-heated as indicated. Exposed horizontally for 100 consecutive hours to a spray of 4 per cent sea-salt solution.

condition of the bar but also the effect of heats up to and including the hardening temperature. The taper-heated bars were Brinelled at $\frac{1}{2}$ -in. intervals. By these figures an approximate measure of the temperature at each point was obtained. The bars were turned and finished with 00 emery. Specimens thus prepared were placed horizontally in the salt-spray machine and subjected to a spray of 4 per cent sea salt solution for 100 consecutive hours. A typical example is shown in Fig. 1.

Individual salt-spray tests were made on standard U. S. Navy test pieces, a $\frac{1}{8}$ -in. round cylinder surmounted and supported by 60° cones, the bottom cone being left attached to a coupon for identification and support. The finish is standardized as 00 American emery dry. These specimens were also subjected to a spray of 4 per cent sea salt for 100 consecutive hours. The results of these tests were obtained by judging the appearance of the corroded specimens and comparing them with standards as follows:

Standard *A* is practically unattacked. One very small rust spot is allowable to grant this rating.

Standard *B* shows local corrosion on one side over approximately one-tenth of its area, the remainder of specimen being bright.

Standard *C* is similar to *B* but shows two spots corresponding to the one on *B*.

Standard *D* is practically rusted all over, showing a general condition of light corrosion.

Standard *E* is badly rusted, covered with deep pits and loose products of corrosion.

Specimens tested in this investigation have been rated in accordance with these standards, qualifying with a plus or minus to indicate intermediate values. Illustrations of these tests are given in Figs. 5, 6, 7a and 7b.

Analyses of the test pieces are given in Table 1.

Corrosion tests were also made on a series of heat-treated pieces by still immersion in an aqueous solution of 5 per cent nitric acid, by volume (Table 2).

A study was made of the microstructure of the metal from the corroded test specimens. An electrolytic method was used in developing the structures. The electrolyte was a 10 per cent solution by volume of hydrochloric acid in alcohol. Three dry cells supplied the current. A strip of stainless material connected to the battery negative was used as one electrode. The specimen was placed in the electrolyte with the prepared face toward the strip at a distance of about one inch.

TABLE 1.—*Analyses of Test Pieces*

Mark	Size	Composition, Per Cent						
		C	Mn	P	S	Si	Cr	Ni
3637-2	1 $\frac{3}{8}$ -in.	0.11	0.38	0.008	0.022	0.25	12.44	0.14
2786-C	1-in. rd.	0.12	0.44	0.015	0.017	0.37	11.97	0.20
3637-K	1 $\frac{1}{2}$ -in. rd.	0.10	0.43	0.012	0.020	0.34	12.82	0.12
3637-Y	1 $\frac{1}{2}$ -in. rd.	0.10	0.39	0.008	0.019	0.43	11.51	0.16
4158-X	1 $\frac{1}{16}$ by $\frac{3}{16}$ -in.	0.11	0.44	0.009	0.023	0.08	11.92	0.24
4903-S	1-in. rd.	0.10	0.47	0.007	0.015	0.47	15.08	0.36

To complete the electrical circuit and start the etching the specimen was touched with a stainless steel stylus, which was connected to the battery positive. There was an evolution of gas from the cathode during etching. The time of etching was kept constant at 20 sec. for the specimens illustrated. The method is adaptable to almost every type of

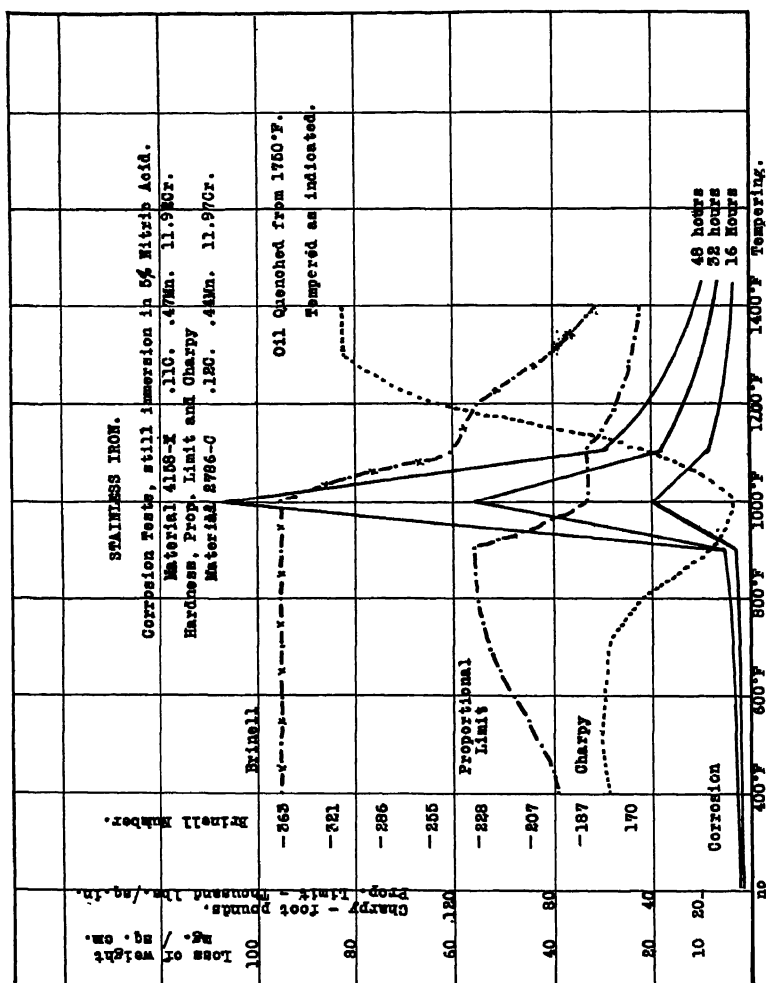


FIG. 2.—CHART OF DILUTE NITRIC ACID SOLUBILITIES GIVEN IN TABLE 2 AND RELATIONSHIP TO SOME TENSILE PROPERTIES OF TABLE 3.

corrosion-resisting steel. It was necessary to repolish and re-etch several times to develop the structures satisfactorily.

DISCUSSION OF TESTS

Tables 3 and 4, with Figs. 2, 3, and 4, tabulate the changes in physical properties of this alloy with variation in heat treatment. It is convenient for purposes of discussion to divide the tempering range into

three groups: (1) "as quenched" and tempered from 400° to 900° F.; (2) 900° to 1100° F.; (3) 1100° F. and higher. The lowest range gives improvement in properties with increase in temperature. The higher chromium (Table 4) increases more markedly in Brinell and tensile than the lower but the trend of the proportional limit is definite in each.

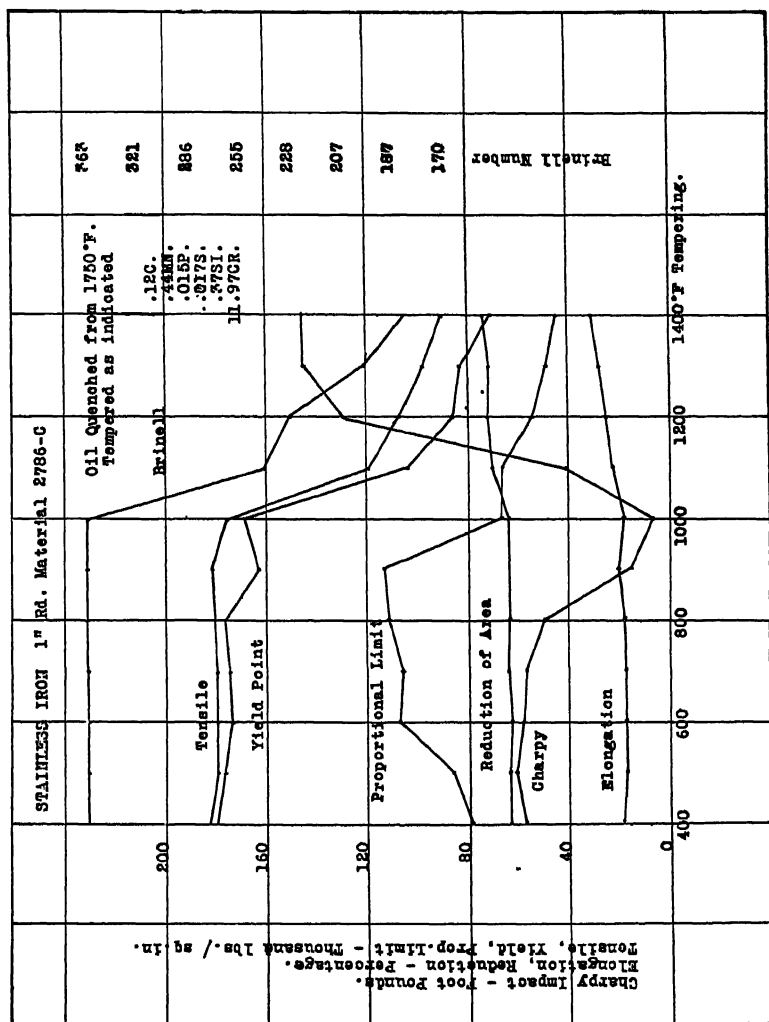


FIG. 3.—CHART OF PHYSICAL PROPERTIES GIVEN IN TABLE 3.

The second range is of primary interest. All values go through sharp changes. This region produces extreme brittleness and is marked by a falling off in proportional limit, hardness, yield point and tensile strength. Small variations in time or temperature of drawing cause

larger changes in physical properties. It is a sensitive range, imparting weakness to the alloy and from a purely physical standpoint should be avoided.

Above 1100° F. the impact value skyrockets with small increments in time and temperature. The tensile properties gradually decrease in a

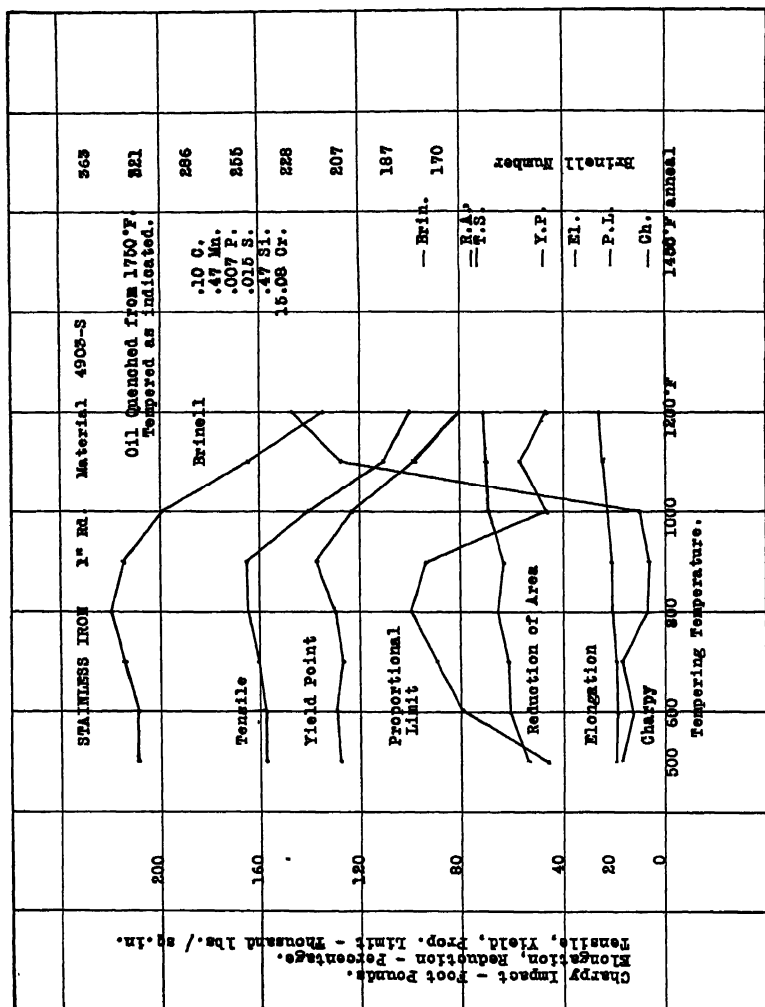


FIG. 4.—CHART OF PHYSICAL PROPERTIES GIVEN IN TABLE 4.

normal way in proportion to increases in temperature, with corresponding improvement in ductility.

Considering the rapid changes taking place in the second tempering range, the extreme susceptibility to corrosion found in the neighborhood

of 1000° F. draw is not remarkable. The maximum corrosive attack is coincident with the break in hardness, tensile and yield point and is slightly preceded by the minimum impact. In every sample tested, regardless of analysis within the range, the corrosion resistance of the alloy has been consistently impaired by drawing at 1000° F. The figures in Table 2 indicate an increase in solubility in nitric acid of 10 to 20 times with a drawing temperature change of 100° F. (from 900° to 1000° F.).

TABLE 2.—*Tests on Heat-treated Pieces**

Corrosion by Still Immersion in 5 Per Cent Nitric Acid, by Volume, at Room Temperature. Material 4158-X. Samples Quenched in Oil from 1750° F. Tempered as Indicated. Abraded on 120 Emery.

Mark	Tempering Temperature, Deg. F.	Brinell Number	Loss of Weight, Mg. per Sq. Cm.			Illustrated in Figures
			16 Hr.	32 Hr.	48 Hr.	
XQ	As quenched	331	1.8	2.1	2.4	8
XQ-4	400	331	1.6	2.0	2.0	9
XQ-9	900	341	2.2	5.3	5.3	10
XQ-10	1000	277	19.6	54.6	103.1	11
XQ-11	1100	196	8.9	18.6	30.7	12
XQ-12	1200	174	6.0	13.3	21.8	13
XQ-14	1450	170	3.2	6.2	9.8	14

* Specimens cleaned and weighed after each test (not reabraded). Corrosion uniform, no pitting.

TABLE 3.—*Physical Properties. Material 2786-C**

Mark	Condition Quenched 1750° F. Oil	Tensile Properties, 1000 Lb. per Sq. In.			Elongation, Per Cent	Reduction, Per Cent	Brinell No.	Charpy Test Ft.-lb.
		Proportional Limit	Yield Point	Tensile Strength				
	Tempered at							
C4	400° F.	78	179	182	18.0	62.8	363	57.0
C5	500° F.	85	176	179	17.1	62.3	363	60.6
C6	600° F.	106	173	179	16.6	61.4	363	58.8
C7	700° F.	105	174	179	17.8	63.3	363	57.9
C8	800° F.	110	176	180	17.7	62.6	363	43.6
C9	900° F.	112	162	181	19.8	63.1	363	15.4
C10	1000° F.	66	168	175	17.3	65.4	363	6.0
C11	1100° F.	66	105	119	21.8	69.9	241	40.7
C12	1200° F.	54	86	106	23.9	71.7	228	128.3
C13	1300° F.	48	82	97	26.6	70.9	187	144.0
C14	1400° F.	44	70	90	29.4	73.5	183	144.3

* Charpy test piece, 0.394 in. square; V-notch, 0.079 in. Tensile tests: 0.505 in. round by 2-in. gage.

It is also worthy of note that the low-tempered samples, XQ, XQ-4 and XQ-9, become passive and lose no further weight after two corrosive increments. XQ-10, which is so extremely poor, as well as XQ-11, 12 and 14, the last having commercial resistance, show progressive corrosion with no indication of becoming passive as far as these tests have gone. The improvement in solubility resistance is marked, however, the higher the temperature.

TABLE 4.—*Physical Properties. Material 4903-S**

Condition Natural	Tensile Properties, 1000 Lb. per Sq. In.			Elonga- tion, Per Cent	Reduction, Per Cent	Brinell No.	Charpy Test, Ft.-lb.
	Propor- tional Limit	Yield Point	Tensile Strength				
Tempered at							
600° F.	64	137	158	14.6	33.8	321	11.3
800° F.	92	141	162	21.0	60.9	341	7.0
1000° F.	47	114	129	24.6	67.0	302	22.6
1200° F.	37	83	101	26.8	70.3	223	76.5
Quenched 1750° F. oil.							
Tempered at							
500° F.	46	128	158	19.2	54.4	321	17.3
600° F.	79	130	158	18.4	60.6	321	13.6
700° F.	89	127	161	19.5	62.2	331	16.7
800° F.	100	130	165	21.2	65.9	341	7.0
900° F.	94	137	166	21.3	64.0	331	6.5
1000° F.	45	123	140	22.4	70.3	302	9.1
1100° F.	56	99	115	25.6	71.5	248	127.3
1200° F.	47	80	100	27.3	71.5	212	146.2

* See Figs. 7a and 7b for salt-spray tests on this material.

The difference in degree of attack is probably more striking in the salt-spray test. The focal point of extreme attack in every case is the 1000° F. draw. The higher chromium alloys, Figs. 5 and 7b, show perfect tests on both sides of the susceptible condition. The difference between these and similar test pieces of Fig. 6 is ascribed solely to the difference in chromium content. The low and high draws of the latter give commercially resistant material but the comparison to the 1000° F. tempered sample is just as striking as in the higher chromium samples.

Differences in structure are found, of course, in examining a heat-treated series. These may be correlated to the physical changes observed. The 4158-X series described in Table 2 is used to illustrate this development. Photomicrographs of these samples appear in Figs. 8 to 14 at 1000 diameters.

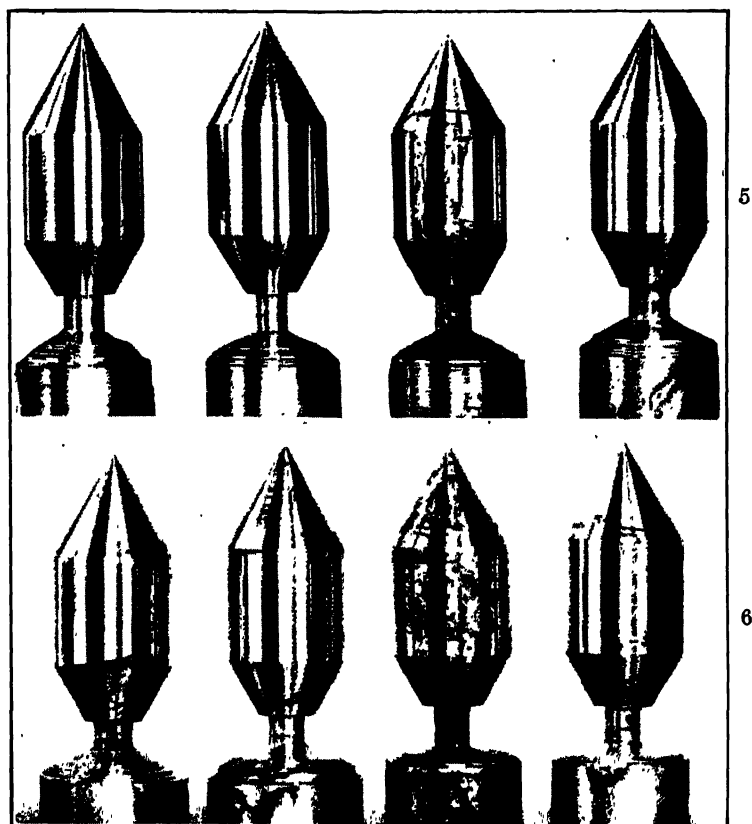


FIG. 5.—PIECES TESTED WITH SALT SPRAY. MATERIAL 3637-K. $\times 1$. (REDUCED $\frac{1}{4}$; ORIGINAL MAGNIFICATION GIVEN.)

Quenched in oil from 1750° F. Tempered as indicated below left to right:

	800° F.	900° F.	1000° F.	1100° F.
Brinell number.....	375	375	352	248
Charpy impact.....	60.6	42.4	14.2	80.4
Salt-spray rating.....	A	A	C	B—

FIG. 6.—PIECES TESTED WITH SALT SPRAY. MATERIAL 3637-Y. $\times 1$. (REDUCED $\frac{1}{4}$; ORIGINAL MAGNIFICATION GIVEN.)

Quenched in oil from 1750° F. Tempered as indicated below left to right:

	800° F.	900° F.	1000° F.	1100° F.
Brinell number.....	363	363	341	241
Charpy impact.....	27.6	27.2	10.2	132.6
Salt-spray rating.....	C	C	D—	C—

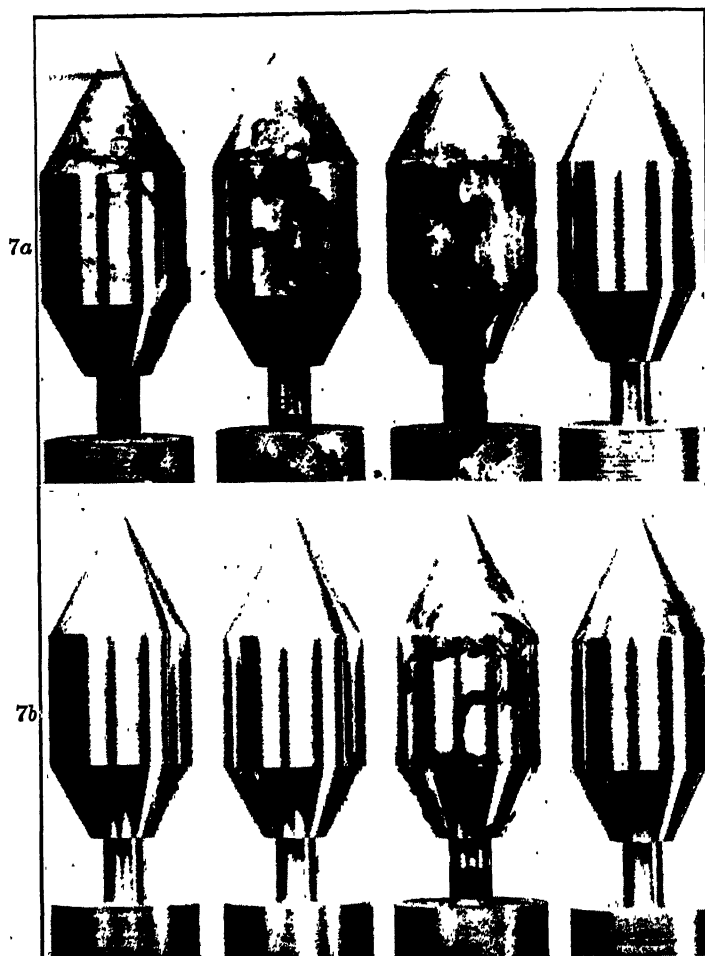


FIG. 7.—PIECES TESTED WITH SALT SPRAY. MATERIAL 4903-S. $\times 1$.

a. As-rolled condition. Tempered as indicated below left to right:

	600° F.	800° F.	1000° F.	1200° F.
Brinell number.....	321	341	302	223
Charpy impact.....	11.3	7.0	22.6	76.5
Salt-spray rating.....	D	D	D	A

b. Quenched in oil from 1750° F. Tempered as indicated below left to right:

	600° F.	800° F.	1000° F.	1200° F.
Brinell number.....	321	341	302	212
Charpy impact.....	13.6	7.0	9.1	146.2
Salt-spray rating.....	A	A	C	A—



FIGS. 8 AND 9.—MATERIAL 4158-X. QUENCHED IN OIL FROM 1750° F. $\times 1000$.

Fig. 8. Sample XQ. No draw. Electrolytic etch.

Fig. 9. Sample XQ-4. Drawn 400° F. Electrolytic etch.



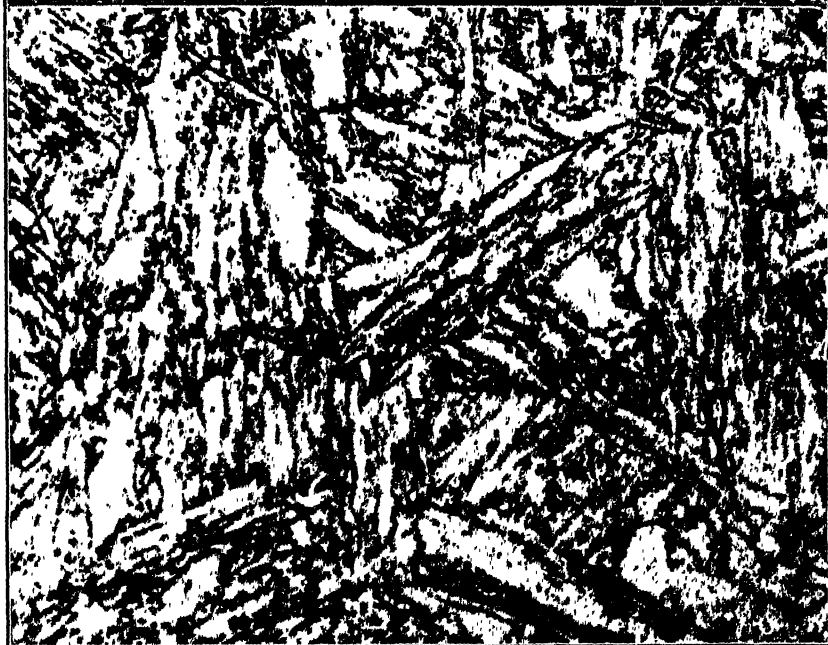
FIGS. 10 AND 11. MATERIAL 4158-X. QUENCHED IN OIL FROM 1750° F. $\times 1000$.

Fig. 10. Sample XQ-9. Drawn 900° F. Electrolytic etch.

Fig. 11. Sample XQ-10. Drawn 1000° F. Electrolytic etch.



12



13

FIGS. 12 AND 13. MATERIAL 4158-X. QUENCHED IN OIL FROM 1750° F. $\times 1000$.

Fig. 12. Sample XQ-11. Drawn 1100° F. Electrolytic etch.

Fig. 13. Sample XQ-12. Drawn 1200° F. Electrolytic etch.

At equilibrium this alloy should consist of a solid solution of chromium in alpha iron (chrome-ferrite) and carbides.³ This condition is most nearly approached in sample XQ-14, annealed (Fig. 14). On heating to 1750° F. for quenching, the lower chromium alloys are entirely chrome-austenite, since on quenching the structure is entirely martensitic. When the chromium or silicon content is rather high, or the carbon low, some

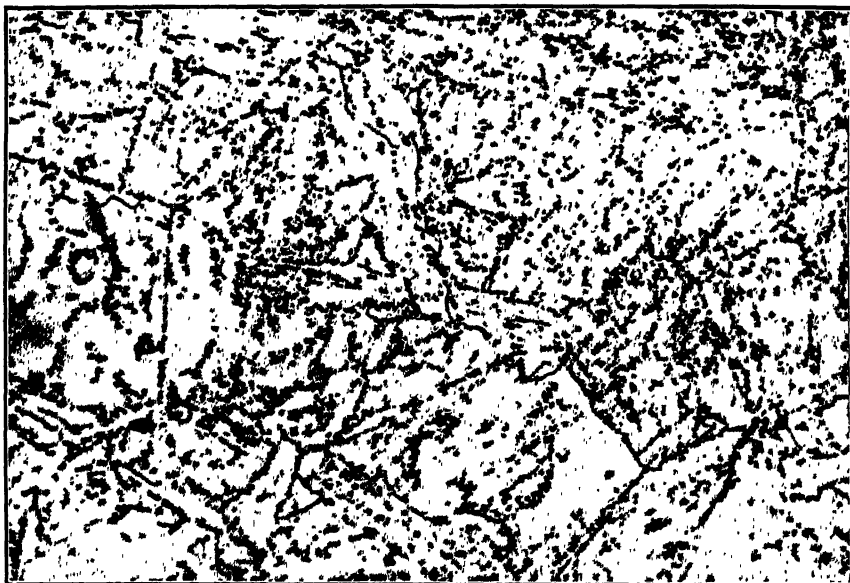


FIG. 14.—MATERIAL 4158-X. SAMPLE XQ-14. QUENCHED IN OIL FROM 1750° F.
 × 1000.
 Drawn 1450° F. Electrolytic etch.

ferrite appears in the as-quenched condition, indicating the presence of the delta phase.⁴ This constituent is soft and causes in the aggregate a lower as-quenched hardness and a lower impact figure in the lower tempering range. The constituent undergoes no structural change except carbon solution on heating and precipitation on drawing. Its presence in small amount has little effect in the drawing range and does not influence the structural breakdown of the chrome martensite. This breakdown is of particular interest because a definite change takes place in this constituent near the tempering temperature at which brittleness and susceptibility to corrosive attack have been found.

The alloy (4158-X) illustrated is purely martensitic as quenched with

³ M. A. Grossman: Nature of the Chromium-iron Carbon Diagram. *Trans. A.I.M.E.* (1927) 75, 214.

⁴ E. C. Bain: Nature of the Alloys of Iron and Chromium. *Trans. Amer. Soc. Steel Treat.* (1926) 9.

no free ferrite (Fig. 8). Drawing at 400° F. (Fig. 9) produces no apparent change in the structure. There is a slight breakdown at 900° F. marked by a darkening of the martensite, which we might call chrome-troostite (Fig. 10). The next sample, XQ-10, drawn at 1000° F. shows a more definite change in structure to the troostitic condition (Fig. 11) and a pronounced precipitation of carbides. From 1100° to 1450° F. further precipitation takes place, forming from the chrome troostite a granular pearlitic structure. On account of the sluggishness of the alloy, the form of the chrome-martensite with the parent austenitic grain is roughly retained and the structure therefore called pseudomartensite.

TABLE 5.—*Summary of Structural Changes and Physical Effects of Tempering Stainless Iron from the Quenched Condition*

Condition Tempering Temperature, Deg. F.	Structural Characteristics	Physical Effects from Previous State	Corrosion Resistance
As quenched	Chrome-martensite	High tensile, yield and impact.	Excellent.
400-800	Chrome-martensite.	Increase in proportional limit.	Excellent.
900	Indication of chrome-troostite.	Drop in impact.	Very good.
1000	Chrome-troostite.	Minimum impact. Low proportional limit.	Very poor.
1100	Granular pearlite (pseudomartensite).	Drop in tensile, yield, proportional limit. Marked increase in impact and ductility.	Good.
1200-1400	Granular pearlite.	Drop in tensile, yield, proportional limit. Increase in impact and ductility.	Very good.
1550-1650?	Mixed.		Very poor.

A further point referred to in the taper-heated tests and in the samples drawn from the natural at low temperatures (Fig. 7a) concerns the importance of a proper quench in this alloy. It will be noted in Fig. 1 that the area marked "partly hardened," estimated temperature 1400° to 1750° F., is subject to attack. The actual temperature range is probably more narrow; *i. e.*, 1550° to 1650° F. This has not been carefully explored. A microscopic examination of this region showed a mixed structure of chrome-martensite-troostite-ferrite and large carbides, in the aggregate, not to maximum hardness, and in a very unhomogeneous condition. While not as marked, the hot-rolled condition is similar. Both are subject to salt-spray attack unless drawn high enough (over 1100° F.) to break down the undesirable structure. At a draw of 1200° F. the cor-

rosion resistance is comparable to the similar sample of Fig. 7b, drawn at 1200° F. after quenching.

SUMMARY

Changes that take place in stainless iron on drawing at various temperatures from the quenched condition are listed in Table 5. In order to clarify the changes taking place we have attempted to diagram results definitely with temperature range. On account of the sluggishness of the changes, however, it must be remembered that one step grades into another comparatively gradually, that the effect of 1 hr., which is the uniform time of draw on all samples reported in this paper, at a certain temperature could probably be obtained by a 2-hr. draw 25° F. lower, while a 4-hr. draw would have the effect of a higher temperature for a shorter time. This is particularly true near the sensitive range about 1000° F. The effects cannot be correlated to the hardness but are more dependent upon the time and temperatures of heat treatment. For example, alloy 4158-X shows 331 Brinell at 400° F. draw. It has excellent resistance to corrosion. Alloy 4903-S shows 321 Brinell at 500° F. draw and has excellent corrosion resistance. If we aimed for this figure on alloy 2786-C we would draw probably at about 1020° F., where the alloy would not only be subject to corrosion but also brittle. The same figure, 321 Brinell, is found on alloy 3637-2 (Fig. 1) in the "partly hardened" area, where it is subject to corrosion. In this way different alloys or the same alloy with different heat treatment will show identical hardnesses but be widely apart in physical properties and corrosion resistance.

It is likely that a small amount of delta iron, which would revert to austenite, or austenite itself, is retained, particularly in the higher chromium alloys, in the quenched condition, although none has been identified microscopically. This would explain the increase in hardness found after low drawing heats. The increase in proportional limit in this range may be due partly to this breakdown and partly to a submicroscopic change in the martensite. Near the peak of the proportional limit curve, a change is first visible microscopically and is associated with the drop in impact. With the complete formation of chrome troostite we have the minimum impact, the point of maximum corrosion and a weakening in proportional limit. With the formation of granular pearlite or pseudomartensite, strength in impact is recovered as well as resistance to corrosion.

It is believed that the fine precipitation which gives rise to the chrome-troostite is the reason for the erratic behavior of this alloy in the tempering range 900° to 1100° F. The loss of corrosion resistance is not believed to be due to the robbing of chromium from solution, since further precipitation produces again a satisfactory condition. The precipitation is not

local, around the grain boundaries as found at times in the austenitic steels, but general, throughout the grain as well as at the boundaries. The local robbing and replenishing theory, advanced for the austenitic steels, does not hold in this case.⁵ The differences found between as-quenched and annealed samples, which are more marked in the lower chromium alloys, may be due to a general depletion of chromium by precipitation of carbides, but the serious condition found at and about a tempering at 1000° F. is due to the condition of the precipitate and its relation to the matrix rather than the amount of precipitate or its effect on the adjoining metal.

CONCLUSIONS

1. Tempering at about 1000° F. from the as-quenched or as-rolled condition produces marked susceptibility to corrosion and weakness in impact in stainless iron. This is accompanied by a lower hardness, a weakening in proportional limit and a general breakdown of the metal.

2. Tensile properties and corrosion resistance of heat-treated stainless iron are excellent when tempered either above or below the susceptible range.

3. Partly hardened or as-rolled steel is likely to be subject to attack unless tempered at 1100° F. or higher.

4. The brittle point and range of lessened corrosion resistance is coincident with the breakdown of the chrome-martensite to chrome-troostite. The formation of a very fine precipitate of carbides at the grain boundaries and within the grains is advanced as the explanation for the phenomena.

It is gratifying to note that the second edition of J. H. G. Monypenny's book (reference of footnote 2), which has just been published, while covering a vastly wider field, discusses in detail and corroborates many points brought out in this paper.

ACKNOWLEDGMENT

The author expresses appreciation to the Crucible Steel Company of America for permission to publish these data; to Dr. J. A. Mathews for helpful suggestions and criticisms; to other associated metallurgists and laboratories of the Crucible Steel Company of America for data and corroboration.

⁵ B. Strauss, H. Schottky and J. Hinnüber: Carbide Precipitation during Tempering of Corrosion Resistant Non-magnetic Chromium-nickel Steel. *Ztsch. f. anorg. u. allge. Chem.* (1930) 188, 309.

H. D. Newell: Influence of Grain Size on Properties and Corrosion Resistance of 18-8 Iron-Chromium-Nickel Alloy for Elevated Temperature Service. *Amer. Soc. Steel Treat. Preprint* 17 (1931).

DISCUSSION

(John A. Mathews presiding)

J. A. MATHEWS, New York, N. Y. (written discussion).—Engineering steels, like people, to be appreciated must be understood. Dislikes and suspicions frequently vanish into thin air upon better acquaintance. It is evident that stainless iron has not met with as large an acceptance in American industry as its merits would seem to warrant when its properties are understood.

When stainless cutlery steel was introduced something over 15 years ago, it was very thoroughly impressed upon the users that the steel must be hardened and polished in order to be satisfactorily resistant to the types of corrosion met with in domestic use in table cutlery.

A little later the low-carbon variety, such as the stainless irons discussed in the paper, was introduced. The idea seemed to become prevalent that these materials did not require heat treatment or that almost any sort of heat treatment would do, and this, as the paper discloses, is far from being the case. The cyclonic change of properties upon tempering of previously hardened stainless iron at about 1000° F.

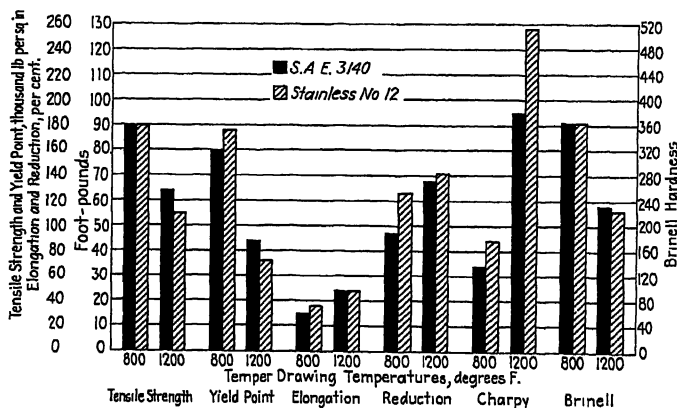


FIG. 15.

makes it practically impossible to work to definite physical specifications necessitating such a tempering, and it becomes apparent that the tempering range between 900° and 1100° should be absolutely avoided. However, when tempering is done at more suitable ranges the properties of the material are such as to lend themselves to a vast number of engineering applications. In the truly American fashion of writing specifications before we know enough about the subject to do so, it has come about that hardness ranges have been specified which can be met only by tempering within the danger zone, and the steel upon being put into use has proved disappointing from both the corrosion resistance and the mechanical point of view.

To show how this steel compares with one of the most widely used S.A.E. steels, when suitably heat-treated, we present a diagram (Fig. 15) comparing stainless iron with S.A.E. 3140 after suitable quenching and tempering at two temperatures; namely, 800° and 1200° F. After the former temperature we obtain very great strength with fair toughness and impact resistance, together with a degree of corrosion resistance which is very useful under many industrial applications. After the 1200° tempering we have a steel still perfectly satisfactory from the corrosion standpoint for many

applications, possessing fair tensile qualities, along with exceptionally good toughness and impact resistance. The diagram does not make clear one other property in which the stainless iron greatly excels S.A.E. 3140; namely, its applicability to deep hardening in large sections. We had occasion to make a very large quantity of 7-in. round stainless iron to be heat-treated to definite mechanical properties. In meeting these it was necessary to draw within the very range that we do not recommend. However, the figures obtained on the test pieces taken from the outside, halfway and center positions on the 7-in. round show conclusively the deep-hardening characteristics of the stainless iron. The proportional limits in the three positions vary between 104,000 and 101,000 lb. per sq. in.; the yield point, between 128,000 and 136,500; tensile strength between 145,000 and 152,000; elongation from 20.3 to 17.6 per cent; reduction in area from 64.5 to 50.3 per cent; and Brinell hardness from 302 to 311.

In several heats it was found that the yield point and tensile strength were actually higher at the center position than at the outside. While this illustrates the capacity for deep hardening, the explanation is probably due to the fact that the time at the tempering temperature was not sufficiently long to bring about complete uniformity throughout this large cross-section.

The characteristics that Mr. Merritt has pointed out as the results of tempering at about 1000° F. should not be looked upon as peculiarities or idiosyncrasies of stainless iron but merely as properties that must be borne in mind in the commercial use of this material. Other steels have critical ranges which must be avoided in their heat treatment. It is generally known, for instance, that many of the high-tensile chromium-nickel construction steels must be quickly cooled from the tempering temperature to avoid impact brittleness. It is also known that many of the S.A.E. steels have a lower impact resistance after tempering at 600° F. than they have when tempered either lower or higher. When these properties are known and suitable heat treatments are applied, depending upon inherent properties, successful use is insured.

W. E. RUDER, Schenectady, N. Y. (written discussion).—As Dr. Mathews has just pointed out, the abrupt change in physical properties occurring at approximately 1000° F., shown by the author's curve on chromium iron, is not peculiar to this particular alloy. About two years ago, in searching for the cause of occasional abnormal brittleness in 3.5 per cent silicon steel sheets, we found that prolonged heating in the range of 1000° to 1200° F. reduced the ductility of such sheets to about one-tenth the normal value. This ductility was restored again by reheating to a temperature of about 1400° F. The maximum rate of embrittlement occurred at about 1200° F. The maximum change in physical condition was accompanied by a 13 per cent increase in electrical resistivity. Except for a possible increase in etching rate, no change in microstructure was observed.

Even though these steels as a rule contain less than 0.06 per cent C, they exhibit the same phenomenon of carbide precipitation in approximately the same range found by Mr. Merritt for the chromium irons. This is another illustration of the importance of what might be called a submicroscopic precipitation of constituents, even though in very small quantities, on the physical properties of an alloy.

P. PAYSON, Harrison, N. J. (written discussion).—The most valuable feature in Mr. Merritt's paper is the presentation of a relationship between microstructure and corrosion resistance of chromium irons. Such a relationship has received insufficient attention in the past. It has been assumed, generally, that the analysis of the alloy, particularly its chromium content, is the only feature to be considered in determining its suitability for corrosion resisting purposes. Even in the most recent

textbook on the subject Monypenny says,⁶ "the corrosion resistance of stainless irons containing more than about 14 per cent chromium is not noticeably affected by any form of heat treatment." Mr. Merritt has shown that this is not true for 15 per cent chromium iron, and Bellinger⁷ has shown that the corrosion resistance of 18 per cent chromium iron is also seriously affected by heat treatment. We have found that not only is 18 per cent chromium iron subject to the same decrease in corrosion resistance when the quenched iron is reheated to about 1000° F., as shown by Mr. Merritt for the low-chromium iron, but that a 26 per cent chromium iron can be so affected by heat treatment that its corrosion resistance will be lower than that of an annealed 12 per cent chromium iron.

The knowledge that microstructure affects corrosion resistance is an important advance in our study of corrosion-resistant alloys, and it is unfortunate that in most of the published data on such alloys the effect of heat treatment has been disregarded. However, before we can arrive at a complete understanding of corrosion-resisting alloys we must answer the question, "Why do some microstructures offer degrees of corrosion resistance different from those of others?" The answer to this question would involve the very fundamental considerations of corrosion phenomena.

It has been established fairly definitely that corrosion is an electrochemical phenomenon associated with the film-forming characteristics of a particular alloy in a particular corroding medium. If we start with this as a basis, it seems obvious that the film-forming characteristics of the alloy are affected by its microstructure. The problem before us, then, is to determine in what way microstructure is associated with film formation, and it is a problem worthy of our best efforts.

⁶ Reference of footnote 1.

⁷ E. St. P. Bellinger: Chrome Iron Indispensable in Nitric-acid Plant. *Chem. & Met. Eng.* (1930) **37**, 691.

A Quantitative Method for the Estimation of Intercrystalline Corrosion in Austenitic Stainless Steels

BY J. J. B. RUTHERFORD* AND ROBERT H. ABORN,* KEARNY, N. J.

(New York Meeting, February, 1932)

It is now well known that troublesome intercrystalline corrosion may occur in austenitic stainless steels following exposure of the metal to a temperature within the range 1000° to 1500° F. (540° to 815° C.). The present paper describes a satisfactory method of estimating the extent of such corrosion, based on the measurement of the electrical resistance of a specimen before and after attack. This new method enabled us to study quantitatively the effect of several factors upon intergranular corrosion in the 18 Cr, 8 Ni type of alloy. The results show that susceptibility to this attack increases with increasing carbon content and grain size and appears to pass through a maximum for certain combinations of temperature of sensitization and period during which the alloy was maintained at that temperature; and are in complete accord with our interpretation of the mechanism of this phenomenon. The method is probably applicable to other metals or alloys subject to intercrystalline attack, such as the aluminum alloys of the duralumin type.

The methods hitherto in use for estimating the degree of intergranular attack fall into three types: (1) microscopic examination,¹ (2) macroscopic examination of fractures, and (3) determination of the time required for complete failure or disintegration.² None of these lends itself very well to a measurement of the extent of corrosion. The first two are qualitative in nature and the third provides an arbitrary value largely dependent on individual judgment, since failure is a progressive phenomenon and not a sudden event. Our experience is that weight-loss determinations, although valuable in some types of corrosion investigations, bear no simple relation to intercrystalline corrosion in this type of alloy, as is to be expected since the phenomenon probably involves only the thinnest films between adjacent metallic grains.

Measurement of electrical resistance has been used recently in the study of some types of corrosion,³ but seems not to have been applied to

* Research Laboratory, United States Steel Corporation.

¹ H. D. Newell: Amer. Soc. Steel Treat. *Preprint* 17 (1931).

² C. A. Scharschu: *Metal Progress* (1931) 20, No. 2.

³ J. C. Hudson: *Proc. Phys. Soc.* (1928) 40, 107; *Jnl. Inst. Met.* (1928) 40, 294.

R. M. Burns and W. E. Campbell: *Trans. Amer. Electrochem. Soc.* (1929) 55, 271.

intergranular corrosion. To this application, for the austenitic stainless steels, it proves to be particularly well adapted. We were led to its use by our interpretation of the way in which the alloy is sensitized to this type of intergranular attack, as follows: When the metal is heated at the appropriate temperature, chromium carbide precipitates at the grain boundaries, which therefore are locally depleted in chromium unless the period of heating has either been so short that no appreciable precipitation has occurred, or so long that the chromium content is equalized by diffusion. If such metal is then subjected to a severe corroding agent, attack will proceed along the grain boundaries, because they are depleted in chromium, leaving the grains themselves substantially unaffected and producing about the grains a nonmetallic (possibly gaseous) envelope of high electrical resistance. As the resistance varies inversely with the conducting area, for a given length of conductor, its measurement before and after a controlled corrosion test should, on this basis, provide a quantitative estimate of the extent of intergranular corrosion so brought about.

The change of resistance is undoubtedly a better criterion of the extent of intercrystalline corrosion than opinion or any "general impression." The index numbers so obtained serve as a measure of the propensity to intergranular corrosion which 18-8 type alloys possess as a result of their previous process or service history. They have proved particularly valuable in estimating the effect upon such susceptibility of the variables in manufacture such as grain size, intermediate temperature treatments, and carbon content.

THE METHOD

The method itself involves three steps: (1) an initial measurement of the electrical resistance of a suitable specimen of the metal; (2) a controlled corrosion treatment imposed on this specimen; and (3) a second measurement of the resistance. Any one of the commonly accepted methods for the measurement of resistance is suitable, the choice depending on the accuracy desired. We have found that a portable potentiometer with a suitable ammeter yields satisfactory results, using as small a current as is consistent with the desired accuracy.

THE SPECIMEN

An important consideration in the choice of a specimen is its form or shape. Wire offers the most convenient form but sections of strip or sheet are readily adapted to the test. If the material is massive it is desirable to machine small test lengths of 2 or 3 in. with uniform cross-section ($\frac{1}{8}$ to $\frac{1}{4}$ in. thick). Whenever comparisons are to be drawn it is important that the specimens be substantially identical in size and shape in order that the opportunity for attack shall be comparable,

and also that the surface be reproducible. This may be achieved by the use of a standard procedure in grinding, machining or etching the surface preparatory to the corroding treatment. Specimens which have suffered severe intergranular attack are often very fragile and require great care in handling to avoid breakage before the final measurement is obtained.

THE CONTROLLED CORROSION TREATMENT

In order to recognize the presence of this condition of susceptibility to intergranular corrosion such reagents as ferric chloride-hydrochloric acid, sulfuric acid, acetic acid, ferric sulfate and copper sulfate-sulfuric acid are often employed. One of the most commonly used tests is to immerse the specimen in a boiling solution containing 10 per cent copper sulfate and 10 per cent sulfuric acid, which appears to attack the grain boundary metal, presumably depleted in chromium, to the exclusion of the grains themselves. We have found, however, that decreasing the copper sulfate content considerably accelerates the attack in alloys containing less than about 0.15 per cent C, and adopted as standard in this work a solution containing 13 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (CP) and 47 c.c. conc. $(\text{CP})\text{H}_2\text{SO}_4$ (1.84 sp. gr.) per liter. The copper content of this solution was found insufficient to prevent general corrosive attack of alloys containing more than about 0.15 per cent C after prolonged carbide precipitation periods; in such cases it was necessary to increase the proportion of copper sulfate.

The period required for appreciable attack is largely a function of the thickness of the specimen and of its previous history. For $\frac{1}{8}$ -in. wire of 18-8 alloy with 0.07 per cent C, the most satisfactory time was 24 hr. in the boiling solution; such a specimen when in the condition of maximum susceptibility to attack will be thoroughly disintegrated within 24 hr. This period was adopted as standard for all the tests described herein; it was lengthened for larger specimens, and shortened in some cases where material was extremely susceptible to attack. In this test it is necessary, of course, to avoid serious concentration changes in the solution through losses by evaporation; this was achieved by the use of a reflux condenser.

It is essential that the ratio of surface area of the specimen to volume of the solution be not too great, as otherwise the solution becomes excessively depleted in copper (by deposition on areas depleted in chromium) causing general corrosive attack by the acid. In general, 250 c.c. of solution per square inch of surface is ample. The retention of a bright specimen surface throughout the test is apparently a satisfactory criterion of a sufficient supply of solution. It is also important that the specimen be thoroughly clean and free of scale, as the presence of oxides on the surface apparently induces excessive copper deposition. Moreover, it appears advisable to support flat specimens on glass rods, as the

contact of such pieces with the bottom of the flask sometimes results in an undue deposit of copper.

Although the external appearance of specimens remains unchanged throughout this corrosion test, subsequent deformation, such as bending, suffices as a qualitative indication of disintegration. If appreciable attack has occurred the surface skin will break and a certain proportion of the loosened grains fall away. The typical appearance of attacked and unattacked wire specimens when formed into a simple helix is shown in Figs. 1 and 2.

A description of the complete test procedure for two specimens, A and D, of $\frac{1}{8}$ -in. wire of 18-8 alloy containing 0.07 per cent C follows. A 12-cm. length of the wire, in a welded chrome-iron container,⁴ was heated at 2100° F. (1150° C.) for 15 min., quenched in water and then held in a lead bath at 1200° F. (650° C.) for a period of 16 hr. This specimen (D) was then removed from the container and polished, finishing with No. 220 carborundum paper. A 10-cm. length was laid off with an automatic center punch and its resistance measured. This specimen was placed in an Erlenmeyer flask with another similar specimen (A) which had been subjected only to the 2100° F. (1150° C.) treatment, and 500 c.c. of the standard copper sulfate-sulfuric acid solution was added. The whole was heated to boiling, under a reflux condenser, for a period of 24 hr., when the specimens were removed, washed and dried, and the resistance again measured. The results of Table 1 were obtained.

TABLE 1.—*Results of Controlled Corrosion Tests*

Specimen	Resistance, Ohms		Percentage Increase
	Original	After Controlled Corrosion Test	
A	0.00955	0.00960	0.5*
D	0.00989	0.3795	3740.

* This change of resistance is within the limit of error of the method.

In specimen D the intergranular bonding material had been so completely removed by the attack that it had entirely lost its metallic "ring" and under the slightest deformation disintegrated to a granular powder. Specimen A, on the other hand, in which no carbide had been precipitated, remained perfectly sound.

This great difference illustrates the sensitiveness of this test procedure. We shall now present other examples of its usefulness in evaluating the

⁴ The use of such a closed container has been found to prevent excessive oxidation during the annealing process and to prevent lead attack, which apparently occurs in nickel-bearing alloys in prolonged contact with lead at temperatures above approximately 1300° F. (700° C.). A lead bath was employed because of the greater uniformity of temperature obtainable.

influence of several factors upon the sensitiveness of the alloy to intergranular corrosion.

EFFECT OF GRAIN SIZE UPON SUSCEPTIBILITY TO INTERGRANULAR ATTACK

The temperature and the time necessary to obtain a thoroughly homogeneous austenite with all the carbon in solution depends upon the composition of the alloy. In general, the higher the carbon and alloy



FIG. 1.—18-8 ALLOY WIRE. SIMPLE COIL TEST AFTER INTERGRANULAR CORROSIVE ATTACK. $\times 5$.

FIG. 2.—18-8 ALLOY WIRE ENTIRELY RESISTANT TO INTERGRANULAR CORROSIVE ATTACK. $\times 5$.

content, the higher the required temperature and the longer the soaking time unless the equilibrium-carbon solubility temperature is considerably exceeded. In this process, however, an important factor enters; namely, grain size. Since this heat treatment is almost always carried out above the temperature of recrystallization, both the temperature and the soaking time have a marked influence on the resulting grain size. Our

observations are in agreement with those of Newell⁵ that, other conditions being equal, susceptibility to intergranular attack increases with grain size. For example, two specimens of similar analysis, after separate homogenizing treatments designed to produce widely different grain size, were held for 16 hr. at 1200° F. (650° C.) and then subjected to the standard 24-hr. controlled corrosion test, with the results of Table 2.

TABLE 2.—*Relation of Grain Size to Intergranular Attack*

Specimen No.	Average Grain Size, Mm.	Increase in Resistance Owing to Intergranular Attack, Per Cent
1	0.0001	4
2	0.004	4980

EFFECT OF TEMPERATURE AND TIME AT TEMPERATURE OF CARBIDE PRECIPITATION

The influence upon intergranular corrosion exerted by the period of heating at the intermediate temperature at which carbide precipitates from the austenitic solid solution has been the object of extensive investigation. The measurements show that an increasing period at a temperature suitable for carbide precipitation results in a rapid increase of intergranular attack. For certain temperatures it appears that this attack passes through a maximum with sufficiently prolonged periods of time at temperature. Presumably under such conditions the chromium-depleted areas have been replenished through a gradual process of diffusion. Typical results are given in Table 3, showing the rapid increase in attack with increasing period of exposure to a temperature of 1200° F. (650° C.).

TABLE 3.—*Relation between Corrosion and Time at Temperature*

0.07 Per Cent Carbon Alloy Specimen	Time Held at 1200° F. (650° F.)	Increase in Electrical Resistance Owing to Intergranular Attack (24-hr. Period), Per Cent
A (control specimen)	0 min.	0.5
B	5 min.	2
C	1 hr.	47
D	16 hr.	3,740
E	168 hr.	11,000 (estimated)*

* This specimen disintegrated to a granular powder before the completion of the corrosion test.

The effect of both time and temperature of intermediate heating upon the resistance index number is shown in Fig. 3 for $\frac{1}{16}$ -in. wire of 18-8

⁵ Reference of footnote 1.

alloy containing 0.07 per cent C, previously heated at 2100° F. (1150° C.) for 15 min. Owing to the very large range of increase in resistance, it is represented on a special nonlinear scale derived from a logarithmic scale.⁶ It is to be remembered that on such a scale small values appear inordinately magnified. This chart shows clearly that susceptibility increases with time at a given temperature and that under this set of conditions it is greatest for a temperature zone of about 1100° to 1250° F.

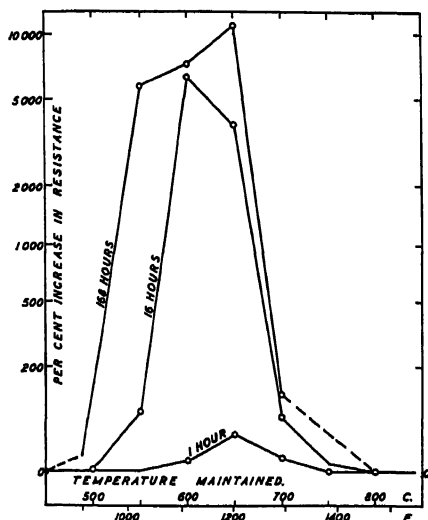


FIG. 3.

FIG. 3.—EFFECT OF TIME AND TEMPERATURE OF INTERMEDIATE HEATING UPON DEGREE OF SUSCEPTIBILITY TO INTERGRANULAR CORROSION IN 18-8 ALLOY CONTAINING 0.07 PER CENT CARBON.

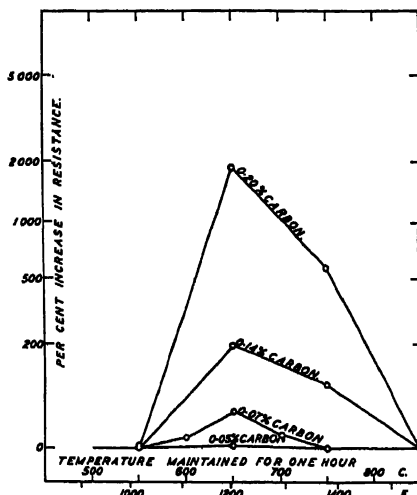


FIG. 4.

FIG. 4.—EFFECT OF CARBON CONTENT UPON DEGREE OF SUSCEPTIBILITY TO INTERGRANULAR CORROSION OF 18-8 ALLOY.

(590° to 675° C.). At temperatures below this zone carbide precipitation probably becomes negligible for the periods involved, while above this zone it appears that chromium diffusion rapidly increases to the point where it is able to keep pace with carbide precipitation.

⁶ The scale was derived from the relation giving percentage increase in resistance:

$$\frac{100(R_F - R_I)}{R_I} = \frac{100R_F}{R_I} - 100$$

where R_I = Initial Resistance, and R_F = Final Resistance. The values obtained from the first term $\frac{R_F}{R_I}(100)$ were plotted on a logarithmic scale. In labeling the scale, however, 100 has been subtracted from the customary logarithmic scale values to take care of the second term (-100). Thus, for example, $\frac{R_F(100)}{R_I} = \frac{3}{1}(100)$ on the true logarithmic scale becomes $300 - 100 = 200$ (or 200 per cent increase) on the labeled scale.

EFFECT OF CARBON CONTENT

The effect of carbon content upon the degree of intergranular attack is illustrated in Fig. 4. These materials were again $\frac{1}{8}$ -in. wire uniformly homogenized, and subsequently heated for 1 hr. at the indicated temperatures. The slight, though really negligible increase in resistance noted in the 0.05 per cent C alloy after the 1200° F. (650° C.) treatment demonstrates the sensitivity of this method. It is believed that such a small change would have failed of detection by any other known method. Evidently an 0.05 per cent C alloy, even when in an accentuated coarse-grained condition, required more than 1 hr. at any carbide precipitation

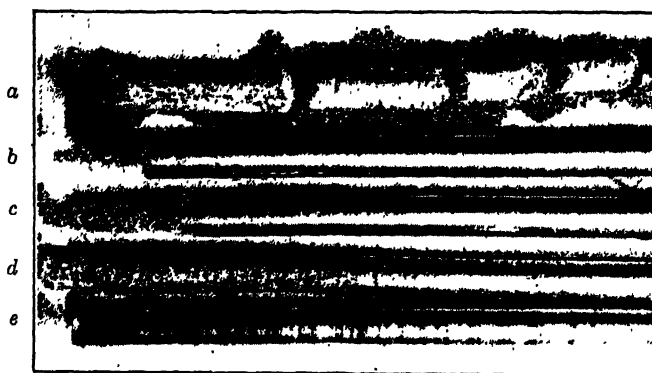


FIG. 5.—CORRELATION OF INCREASE IN ELECTRICAL RESISTANCE WITH RESIDUAL CORE OF UNATTACKED METAL REMAINING AFTER INTERGRANULAR ATTACK. $\times 2$.

Increase in electrical resistance
a. 4000 per cent. d. 4 per cent.
b. 2700 per cent. e. 0 per cent.
c. 155 per cent.

temperature to show any appreciable intergranular attack during the standard test period. It seems obvious that such material possesses a great advantage over higher carbon alloys for welding purposes, with excellent expectation of freedom from subsequent intergranular attack, achieved without the necessity of any heat treatment after welding.

EVALUATION OF METHOD

The observed increase in electrical resistance is a direct measure of the intergranular attack in a controlled corrosion test. This behavior is believed to constitute a reliable test for the probable intergranular corrosion of these austenitic stainless steels under normal service conditions over long periods. Loss in weight of material during corrosion treatment can sometimes be correlated with change in electrical resistance. The conditions controlling the former, however, are complex and the

percentage loss in weight over reasonable periods of time is so small as to be generally valueless. Specimens subjected to this test and subsequently twisted to failure revealed an unattacked core, the diameter of which correlated satisfactorily with what might have been expected from the resistance test. Whenever an appreciable increase in resistance was observed, there was visible attack on the twisted specimen. Fig. 5 shows the residual core of unattacked metal after various degrees of disintegration and the corresponding percentage increase in resistance is indicated.

The three outstanding advantages of this method would seem to be that it is (1) quantitative in nature, (2) rapid, and (3) that it has wide applicability with respect to the many variables possible in the production, treatment and service of these steels. A possible disadvantage lies in the unusual care necessary to obtain a uniform heat treatment and preparation of the specimen surface when comparisons are to be drawn. It is not uncommon to find deviations of 10 per cent in results on duplicate specimens, but in view of the magnitude of the potential range of increase in resistance, this is obviously not serious.

CONCLUSION

The change in electrical resistance, which occurs during intergranular corrosion attack, has been made the basis of a quantitative method for the estimation of the degree of such attack in austenitic stainless steels. The method has been developed into a significant routine test for the measurement of susceptibility to intergranular corrosion in such alloy steels arising from their composition or their previous history.

ACKNOWLEDGMENT

The authors are indebted to Mr. C. H. F. Cottee for his work on the portion of the investigation dealing with the effect of carbon content.

DISCUSSION

(John A. Mathews presiding)

J. K. FINDLEY, Dunkirk, N. Y. (written discussion).—The authors have presented in a few pages the condensed data on a constructive experiment. It is quite possible that the change in electrical resistance could be made a basis of measurement of susceptibility of intergranular corrosion. I believe it could be used to determine whether or not 18-8 metal has been sufficiently annealed after hot working to insure the best possible physical properties in the cold-drawn or cold-rolled products made from the hot-worked materials. There may be, however, a little difference between the specific electrical resistance of two different heats of 18-8 of as nearly as possible identical analysis. That is, fully annealed pieces from one heat may show a resistance of 69 microhms per cubic centimeter and the other heat 71 or 72 microhms per cubic centimeter, yet the latter will not show any susceptibility of intergranular corrosion. The method of Messrs. Rutherford and Aborn should be a valuable aid in the sidetracking of any 18-8 metal during processing that would be susceptible to intercrystalline corrosion.

V. N. KRIVOBOK, Pittsburgh, Pa. (written discussion).—The interest displayed by workers in the field of metals for chrome and chrome-nickel alloys is indeed encouraging. It is not an exaggeration to say that had we been more careful and had we studied the alloys of this type more thoroughly before they were offered to the engineers, a great deal of misunderstanding, many difficulties and unjustified, hasty conclusions would have been avoided; for it must not be forgotten that where more caution has been exercised in placing these alloys under suitable conditions of service no difficulty has been experienced and alloys are still used with efficiency.

It is quite true that practically every paper published on the subject during the past two or three years has dealt, at least in part, with the familiar question of "decomposition" of chrome-nickel alloys. While in most of these publications the material investigated seems to have been limited to the consideration of so-called 18-8 type (18 per cent Cr, 8 per cent Ni, low-carbon alloy), yet it is true that phenomenon of decomposition is not confined to this type only. It is, therefore, necessary that our efforts should be concentrated—if we want to continue to use chrome-nickel alloys in installations where their use is prohibited at present—upon a study of the process of decomposition and its prevention. The theoretical side of this phenomenon is supposedly well understood, although, of course, there still are some dissenting opinions. We have reached that stage in our work where it is imperative to know how to prevent such decomposition. Furthermore, should encouraging results be achieved, it is essential to have at our disposal simple means by which decomposition phenomenon could be detected and its influence ascertained. The interest in the publication by Messrs. Rutherford and Aborn, as well as in that of Mr. Payson,⁷ is, therefore, obvious. These gentlemen offer for our consideration two methods for detecting and measuring decomposition. The method of Rutherford and Aborn—that of precise measurements of electrical resistance—is, to the best of my knowledge, used for the first time, while the one proposed by Mr. Payson is an ingenious and much simplified modification of the method already extensively used. I surmise that Messrs. Rutherford and Aborn desire to present to their colleagues a new method which served them well for a certain specific purpose. Whether this method could be applied generally and help with the problems of decomposition remains to be seen. The results, as I found them in the paper, deal only with chromium-nickel alloys of one type, namely 18-8, although interesting but not new results concerning the dependence of decomposition on grain size and carbon content are included.

Simple magnetic methods were encouraging when they were first applied to the study of this problem. Later, however, it was found that the magnetic susceptibility of certain modified chromium-nickel alloys is not the measure of resistance to intergranular corrosion. This is mentioned by Mr. Payson, and prior to that has been spoken of by several other investigators. Consequently, it is to be awaited with interest what Messrs. Rutherford and Aborn have to say in regard to the applicability of their method to alloys of other types. Even should this method fail, as others have, it will not detract from its value as a scientific tool to be applied to certain alloys.

J. H. G. MONTPENNY, Sheffield, England (written discussion).—The test method described by Rutherford and Aborn appears to have very interesting possibilities providing its true significance is kept in mind. So far as the writer is able to understand the matter, the test gives a numerical indication (and a very sensitive one) of the depth to which intergranular attack has proceeded in a test sample under standardized conditions of corrosion. Presumably if these conditions were changed—that is, if the duration of corrosion was doubled or trebled, the increase in resistance of

⁷ See page 306.

samples slightly attacked would be correspondingly more marked. In the extreme case, it would appear that if corroded for a sufficiently long time any sample whose structural condition made it subject to intergranular attack would be disintegrated entirely and hence show several thousand per cent increase in electrical resistance.

The test as described, therefore, gives a measure of the rates of attack of steels which are liable to suffer intergranular attack owing to undesirable structural conditions. But is this really the information desired by makers of corrosion-resisting steels, by those who fabricate the latter into chemical plant, or by the chemical engineers who are to operate the plant?

It is probably safe to say that the average chemical engineer who requisitions plant in corrosion-resisting steels desires plant which is entirely free from any tendency to develop intergranular attack, and he would not be greatly concerned in discriminating between two steels whose rates of intergranular attack (in the fabricated condition) were such as to lead to his plant being more or less disintegrated in six months or a couple of years respectively. If he were wise, he would reject both, or else insist that the fabrication methods employed in constructing the plant be so altered as to ensure the latter being in a condition free from any tendency to intergranular attack.

Consider, for example, the construction of welded vessels in the ordinary 18-8 steels. It is common knowledge that such vessels, if used in the welded condition, are liable to suffer intense intergranular attack in those areas where the material has been heated to 600° to 700° C, or thereabouts, during the welding operation. It is known, further, that the time during which the steel needs to be kept at 600° to 700° C. in order to render it liable to intergranular attack is very short; generally less than one minute. Now the aim of the steelmaker is to produce steels which are still entirely free from any tendency to intergranular attack after they have been heated at 600° to 700° C., or thereabouts, for a time so much longer than that required by any commercial welding operation as to provide an adequate margin of safety. Obviously, then, the factor which should be used in assessing the relative merits of different steels in this respect is the maximum time that each may be held in the range 600° to 700° C., without producing the least tendency to suffer intergranular attack. It is not at all certain that such information would be given by a test indicating the rate at which corrosion takes place when this maximum safe time has been exceeded in all the steels tested.

If this idea is correct, the variable, in testing steels for intergranular attack, should be the time they are heated in the carbide precipitation range; the corrosion test should be looked upon in the light of a detector whose function is to make evident the least tendency for intergranular attack to occur, rather than to measure the rate at which this attack does occur when the steel is in a structurally bad condition. While one would readily agree that a very rapid corrosion rate indicates a bad structural condition and, further, that a sample possessing such a rate of attack is likely to have been heated in the carbide precipitation range for a time considerably exceeding its maximum safe period, it is not safe to conclude that the reciprocals of the rates of attack of different specimens are related in a simple manner with the maximum periods during which they may be safely held in the carbide precipitation range.

This idea finds expression in the methods of test adopted, for example, by the British Air Board, and by some of the large chemical manufacturers in Great Britain. In these tests, the corrosion test is made severe, and the slightest indication of intergranular attack leads to the rejection of the steel. The British Air Board tests, for example, specify 72 hr. boiling in a solution containing approximately 10 per cent each copper sulfate and sulfuric acid; the test samples are then bent through 180° over a radius equal to one-half their thickness, when the slightest tendency to intergranular attack leads to visible cracking of the tension surface.

From this standpoint the electrical resistance method described by the authors has the merit that it appears to be very sensitive, and hence able to detect a very slight amount of intergranular attack. The writer would suggest, however, that the corroding period of 24 hr. could, with great advantage, be increased to say 72 hr. By this means the chance of samples only slightly subject to intergranular attack escaping detection would be reduced.

In discussing the mechanism of intergranular attack, the writer has no desire to belittle the work done by Messrs. Rutherford and Aborn; he merely wishes to emphasize that the rate at which the carbide precipitation is produced is the more important variable. When both variables are taken into account, as in Fig. 3, the results are likely to be of very considerable value. Fig. 3, for example, indicates definitely that reduction of carbon content to 0.07 per cent does not by any means provide an ideal heat-resisting alloy, a result which would be expected from the work of Dr. Aborn and Mr. Bain regarding the solubility of carbon in these austenitic steels at various temperatures. One might suggest that a series of experiments, similar to those detailed in Fig. 3, but carried out on materials of still lower carbon content (*e. g.*, the one containing 0.05 per cent referred to in Fig. 4) would provide very interesting data. Perhaps the authors would include such tests in their future investigations.

J. J. B. RUTHERFORD AND R. H. ABORN (written discussion).—Mr. Findley has called attention to a very interesting point. It is assumed that he refers to the change in electrical resistivity as a possible basis of measurement of susceptibility to intergranular corrosion without the actual performance of a corrosion test. This has been investigated to some extent but without satisfactory results. The data in Table 4 give some idea of the lack of correlation between the observed change in resistivity due to heat treatment and the observed change in resistance during subsequent immersion in $\text{CuSO}_4\text{:H}_2\text{SO}_4$ solution. The change in resistivity is related in a complex manner to the chemical and physical state of the austenitic solid solution and any other phase, such as carbide, which may be present, whereas the change in electrical resistance is a direct function of the intergranular corrosion produced in a controlled test.

TABLE 4.—*Comparison of Change in Electrical Resistance of 18-8 Alloy by Heat Treatment and by Intergranular Corrosion*

Heat Treatment 15 Min. at 1150° C. Followed By	Electrical Resistivity, Ohms per Cu. Cm. at 25° C.	Comparative Change in Resistance during Subsequent Corrosion in $\text{CuSO}_4\text{:H}_2\text{SO}_4$ Solution, Per Cent
16 hr. at 550° C.	70.6×10^{-8}	0
170 hr. at 550° C.	70.4×10^{-8}	40
170 hr. at 650° C.	70.8×10^{-8}	1400
	70.3×10^{-8}	4000

The thoroughgoing discussion offered by Mr. Monypenny is indeed welcome. The standardization of this method was evolved merely for convenience in comparison of different alloys. Since the publication of this paper, the authors have done some little work on alloys which were fairly resistant to the $\text{CuSO}_4\text{:H}_2\text{SO}_4$ solution, and with which the duration of corrosion had to be prolonged to periods even up to 550 hr. Fortunately there is a distinct mathematical relationship between rate of corrosion and increase of electrical resistance.

It has been the authors' experience that relatively few of the commercially available austenitic stainless steels are absolutely immune to intergranular attack in a

prolonged $\text{CuSO}_4\text{:H}_2\text{SO}_4$ test, after having been exposed to temperatures in the range 600° to 700° C. In view of this, these alloys may conveniently be graded according to rate of attack, and in developing improvement the first aim must be to place this rate at a minimum.

The method of test adopted by the British Air Board is of interest, as it indicates that 72 hr. in a solution of 10 per cent $\text{CuSO}_4\text{:}10$ per cent H_2SO_4 may be taken as a fair criterion of possible atmospheric conditions. For the chemical industry, however, it appears that a more drastic criterion is necessary. This may be obtained by decreasing the CuSO_4 content or increasing the immersion period, or both. The effect of decreasing the CuSO_4 content is shown in Table 5, comparing susceptibility of two 18-8 alloys to intergranular corrosion in two different solutions.

TABLE 5.—*Increase of Resistance after 24 Hours Immersion*

Carbon, Per Cent	Heat Treatment	1% $\text{CuSO}_4\text{:}8\%$ H_2SO_4 , Per Cent	10% $\text{CuSO}_4\text{:}10\%$ H_2SO_4 , Per Cent
0.05	16 hr. at 650° C.	24	4
0.14	1 hr. at 750° C.	95	26

^a Standard solution used by authors.

The effect of increasing the immersion period is shown in Table 6. This alloy was unattacked after 72 hr. in solution, but subsequently developed intergranular corrosion.

TABLE 6.—*Effect of Increasing Immersion Period*

18-8 Alloy Held 1 Week at 575° C.

Immersion period, hr.....	188	255	525
Increase in resistance, per cent.....	0	4	55

It appears to the authors that in order to find the maximum period of exposure to elevated temperature which an alloy can endure before becoming susceptible to intergranular attack, the logical method is to extrapolate figures indicating severity of attack, to the maximum exposure period at which the alloy shows no attack. For this purpose one must know the rate of attack.

Dr. Krivobok's remarks are characteristically stimulating and always appreciated. It may be stated that the electrical resistance method has been applied with equal success to the study of austenitic and semi-austenitic stainless steels comprising a wide composition range.

A further important use of this method has consisted in evaluating various schemes for the *elimination* of intergranular corrosion, in which we have now been entirely successful.

Prevention of Intergranular Corrosion in Corrosion-resistant Chromium-nickel Steels

By P. PAYSON,* HARRISON, N. J.

(New York Meeting, February, 1932)

INTERGRANULAR corrosion in corrosion-resistant chromium-nickel steels has been widely discussed in the last few years. So far as the author knows, nothing has been published which definitely shows that this tendency can be eliminated, although suggestions have been made that a remedy is possible if certain specifications are satisfied.

Strauss, Schottky and Hinnüber¹ suggested an increase in chromium content to an extent that would prevent the impoverishment of chromium on carbide precipitation sufficient to cause impaired corrosion resistance in the matrix.

Pilling² suggested an increase in nickel, so that the stability of the austenite matrix would be increased.

Aborn and Bain³ say that "intergranular attack—may be eliminated by preventing carbide precipitation (*e. g.*, by lowering the carbon content or somehow raising its solubility) or by precipitating it permanently under conditions which will not remove chromium from solid solution so drastically at any points." In a later paper Aborn and Bain⁴ state that many different metallic elements, tungsten, vanadium, copper, aluminum, molybdenum, titanium and zirconium, have been added in small percentages to increase the stability of these alloys, but that it has been reported that according to the copper sulfate test these added elements act only to retard the intergranular corrosion, and that increased nickel and chromium contents have similar effects.

Newell⁵ showed that the lower the quenching temperature before reheating, the less severe was the intergranular attack.

* Research Department, Crucible Steel Co. of America.

¹ B. Strauss, H. Schottky and J. Hinnüber: Carbide Precipitation During Tempering of Corrosion Resistant Non-Magnetic Chromium-Nickel Steel. *Ztsch. f. anorg. u. allg. Chem.* (1930) 188.

² N. B. Pilling: Some Effects of Nickel Content in Austenitic Iron Chromium-nickel Alloys. *Proc. Amer. Soc. Test. Mat.* (1931) 30, Pt. 2.

³ R. H. Aborn and E. C. Bain: The Nature of the Nickel-chromium Rustless Steels. *Trans. Amer. Soc. Steel Treat.* (1931) 18, 837.

⁴ R. H. Aborn and E. C. Bain: The Wrought Austenitic Alloys. Symposium on Effect of Temperature on Properties of Metals. *Amer. Soc. Mech. Engrs. and Amer. Soc. Test. Mat.* (1931).

⁵ H. D. Newell: Influence of Grain Size on the Properties and Corrosion Resistance of the 18-8 Iron-Chromium-Nickel Alloy for Elevated Temperature Service. *Preprint* 17, *Amer. Soc. Steel Treat.* (1931).

Krivobok⁶ says: "Our efforts towards combating such decomposition (*i. e.*, susceptibility to intergranular attack) should be directed toward (a) increasing the solubility of carbides at all temperatures; (b) producing a matrix which would resist migration of carbides to the grain boundaries and their agglomeration; (c) producing a matrix which in itself (even if carbides have separated) would resist corrosion; (d) forming carbides of elements other than chromium; (e) rendering the matrix less susceptible to phase change." He experimented with small additions of copper, cobalt, molybdenum and silicon, singly and in combination, but arrived at no satisfactory solution to the problem.

The present author also experimented with various additions to the chromium-nickel corrosion-resistant steels but with a somewhat different purpose in mind from the suggestions cited. It is a coincidence that the author's purpose is most nearly defined by Krivobok's suggestion *b*. But Krivobok placed considerable emphasis on the association between magnetic susceptibility and intergranular corrosion, whereas the present author places considerable emphasis on the association between magnetic susceptibility and *resistance* to intergranular corrosion.

PURPOSE OF INVESTIGATIONS

Intergranular corrosion is of importance, first, in welded structures which are to be in contact with electrolytes at low temperatures, and, second, in structures that may be exposed to active electrolytes after being subjected for a considerable period of time to elevated temperatures, say, 1000° to 1600° F. The present work deals mainly with the effect of short-time heating over the range 1000° to 1600° F., such as might be encountered in the heating of the metal adjacent to the weld during the welding operation. Heating for 10 min. at temperature was considered satisfactory for this purpose, although it is assumed that in most welding operations the time at temperature would be considerably less than 10 min. It was felt that if materials could be developed that would be resistant to intergranular corrosion after reheating for 10 min. over the temperature range 1000° to 1600° F., such materials could be used satisfactorily for welded structures to be exposed to active electrolytes, and a considerable advance would be made in the availability of corrosion-resistant steels for chemical equipment.

PROCEDURE

A large number of modifications of the 18 chromium, 8 nickel analysis was made with the purpose of obtaining compositions containing an appreciable amount of ferrite. The reason for this will be explained

⁶ V. N. Krivobok: Further Studies on Chromium-Nickel-Iron and Related Alloys. *Preprint*, Amer. Soc. Steel Treat. (1931).

later. Other modifications not containing ferrite were also made up for comparison tests. Most of these were rolled to sheets about $\frac{1}{32}$ to $\frac{1}{16}$ in. thick. In addition, samples of various commercial heats were investigated.

For determining the susceptibility to intergranular attack, the solution proposed by Strauss,⁷ and hereinafter called the Strauss solution, was used. This solution was made up of 10 per cent sulfuric acid and 10 per cent copper sulfate in water, and used at boiling temperature. The samples were tested in this solution in flasks fitted with condensers, the solution being changed every two or three days whenever the tests were made over a fairly long time. In some instances, the tests were continued

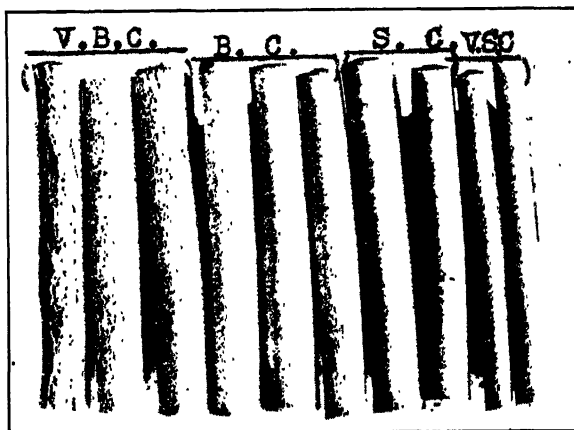


FIG. 1.—TYPICAL APPEARANCES OF BENDS ON SAMPLES ATTACKED IN STRAUSS SOLUTION. $\times 1\frac{3}{4}$.

V. B. C. means very badly cracked; B. C., badly cracked; S. C., slightly cracked; V. S. C., very slightly cracked.

for approximately 1000 hr., but in most cases a much shorter time in the Strauss solution was considered sufficient for the purpose.

It is not at all easy to measure the degree of intergranular attack. The ideal method is to measure the depth of penetration in a carefully prepared microsection. When there are many samples to be examined, as there were in these investigations, the task of preparing microsections becomes enormous. Furthermore, when a sample is severely attacked intergranularly, it is difficult to prepare the microsection for a measurement of depth of penetration because the grains at the surface fall out during the preparation of the sample, and consequently it is not easy to establish a datum line from which to measure the depth of penetration. When a sample is intergranularly attacked, polishing tends to smear the metal into the very thin cracks at the grain boundaries and thus obliterate them. Because of this it is frequently necessary to etch and polish the

⁷ Reference of footnote 1. See also correction on page 332.

sample several times in order to make sure that the cracks exist. When the sample is [comparatively thick and the attack is not very severe, examination of a properly prepared microsection is practically the only method to use for determining depth of penetration. With sheet samples, however, intergranular attack can be much more readily determined. Strauss pointed out that when a piece of sheet has been intergranularly attacked it loses its metallic "ring"; that is, it sounds dull or "dead" when dropped on a hard surface. It was found that the degree of intergranular attack could be readily, although perhaps not very accurately, determined by comparing the metallic ring of an unattacked piece of sheet with that of an attacked piece. When a sample is severely attacked, this "ringing test" is satisfactory, but when there is only a partial attack the ringing test is not safe. A bending test was finally adopted to supplement the ringing test. This consisted of bending in a vise the samples which had been subjected to the Strauss solution and noting the degree of cracking at the bend. If the sample broke off in this bending test, the attack was considered complete; if the sample did not break it was graded "very badly cracked," "slightly cracked," etc., as shown in Fig. 1. Microscopic examination was resorted to whenever the sample was not of sheet thickness.

For measurement of magnetic susceptibility, a "magnetic balance" was used (Fig. 2). This is an adaptation of devices shown in various physics textbooks. It consists of an inexpensive but strong balance sensitive to at least 0.1 g. The sample pan 3 is made from a thin disk of nonmagnetic material. The balance is placed on a table so that this pan, when balanced, just clears the pole piece of the single coil electromagnet 4. The current to the electromagnet is controlled by rheostat 7 and milliammeter 6. When a test for magnetic susceptibility is to be made, the sample to be tested is placed at the center of pan 3 and its weight determined to within 0.1 g. by adding balance weights to pan 5. A definite constant current is then applied to the electromagnet. If the sample is at all magnetic, it will be

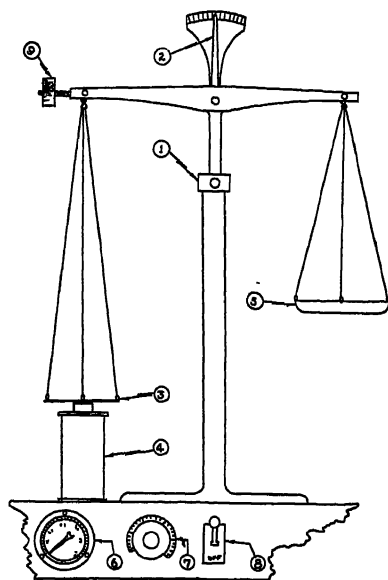


FIG. 2.—MAGNETIC BALANCE.

1. Balance frame and arm.
2. Indicator arm.
3. Specimen scale pan.
4. Magnetizing solenoid.
5. Weight scale pan.
6. Milliammeter.
7. Control rheostat.
8. Switch.
9. Counterbalance.

attracted to the electromagnet, and the greater the magnetic susceptibility of the sample, other things being equal, the greater will be the pull toward the electromagnet. By adding balance weights to pan 5 while the current is passing through the coil, until pan 3 with the sample on it just pulls clear of the core of the electromagnet, the magnetic pull, or magnetic susceptibility, can be readily determined. Since early in the use of this instrument it was found that the magnetic pull is not independent of size and shape of the sample being tested, its use must be confined to samples of similar size and shape. However, experience has shown that for samples of similar size the magnetic balance is highly satisfactory for determining comparative magnetic susceptibility of slightly magnetic materials, and "grams pull" is a satisfactory measure of magnetic susceptibility.

ASSOCIATION BETWEEN MAGNETIC SUSCEPTIBILITY AND RESISTANCE TO INTERGRANULAR CORROSION

Before presenting the results of the author's investigations it is necessary to point out an important difference between the magnetic susceptibility which may be present in 18-8 alloy when it is in a condition susceptible to intergranular attack, as pointed out by Strauss and by Krivobok, and the magnetic susceptibility developed in modifications of the 18-8 analysis by suitable additions such as used by the author to develop steels resistant to intergranular attack. The 18-8 analysis when cooled rapidly from about 1850° to 2100° F., which is the usual treatment used for annealing this steel, and which shall hereafter be referred to as "annealing," is nonmagnetic; that is, austenitic. When this annealed steel is reheated within the range of about 1100° to 1400° F. for a considerable time it may develop appreciable magnetic susceptibility, and in this magnetic condition it may be subject to intergranular corrosion. Both Strauss and Krivobok showed that the presence of a magnetic phase is not necessary for intergranular corrosion, since steels other than 18-8, specifically the higher nickel steels, are still subject to intergranular corrosion even though no magnetic phase is present, but Krivobok indicated that the presence of the magnetic phase resulting from the decomposition of austenite plays an important part in the susceptibility to intergranular corrosion.

It was found early in the author's investigations that the addition of some elements in sufficient quantities to develop ferrite in the steel when rapidly cooled from 1850° to 2100° F. made the steel highly resistant to intergranular attack. The magnetic phase thus present is different from that discussed by the previous authors in that it depends on composition rather than on the decomposition of unstable austenite, as does reheated 18-8 alloy. It is present before any reheating takes place. Bain and others have shown that by varying the ratio between chromium and

nickel in the corrosion-resistant steels, the resulting structures may consist of ferrite alone, as in the plain high-chromium steels, or austenite alone, as in the high-chromium nickel steels such as 18 per cent Cr, 20 per cent Ni, or a combination of ferrite and austenite, as in a steel of, say, 22 Cr, 6 Ni. The author has found that by adding to the standard 18-8 analysis enough silicon, molybdenum, vanadium or other elements forming "loop diagrams" with iron, the same effect is produced as is found in the 22 Cr, 6 Ni steel, for example; namely, the development of a two-phase structure, austenite and ferrite. In these two-phase chromium-nickel steels the resistance to intergranular corrosion is very much higher than in the standard 18-8 alloy of the same carbon content. The presentation of the data which prove this will follow; then a hypothesis will be offered to account for this added resistance.

TABLE 1.—*Analyses of Sheet Samples*

Steel	Modification	Composition, Per Cent							
		C	Ni	Cr	W	Mo	Si	Ti	V
1	Regular.....	0.09	9.08	17.95					
2	High chromium.....	0.13	7.20	21.04					
3	Low tungsten.....	0.08	8.20	19.87	0.80				
4	Medium tungsten.....	0.09	8.15	20.75	1.21				
5	High tungsten.....	0.10	8.27	20.50	4.02				
6	High tungsten.....	0.16	8.08	20.56	4.02				
7	Low molybdenum.....	0.09	9.70	18.42		0.99			
8	Medium molybdenum.....	0.09	9.70	18.94		1.87			
9	High molybdenum.....	0.10	8.20	20.18		3.38			
10	High molybdenum.....	0.17	8.36	19.96		3.25			
11	High silicon.....	0.12	8.20	20.82			3.92		
12	Titanium.....	0.09	9.89	17.90				0.70	
13	High chromium-titanium.....	0.10	8.05	21.12				0.87	
14	Low vanadium.....	0.12	8.52	19.30					0.66
15	High vanadium.....	0.12	8.26	19.11					1.88
16	High chromium-vanadium.....	0.13	8.30	22.01					0.78

EXPERIMENTAL DATA

A series of steels of the compositions shown in Table 1 was made up in 30-lb. ingots and rolled to sheets about 0.030 to 0.040 in. thick. These were tested according to the following procedure. Samples about 1½ by 1 in. were quenched in water from 1900° and from 2100° F. Individual samples of each grade and each quenching temperature were then reheated for 10 min. at temperature at 1100° to 1600° F. in 100° intervals. All samples were then subjected to the boiling Strauss solution for various lengths of time. At frequent intervals the samples were tested by the ringing test, and whenever a sample tested "dead" it was removed from the test, the remaining samples being replaced in fresh solution for further exposure. On some steels the tests were continued up to about 100 hr. exposure, on others up to about 200 hr., some up to 400 hr., two

TABLE 2.—Bend Test on Sheet Samples Subjected to Strauss Solution after 10 Minutes at Reheating Temperature

Steel No.	Modification	Quench. Temp.	Magnetic Susceptibility	Reheating Temperature															
				1000° F.		1100° F.		1200° F.		1300° F.		1400° F.		1500° F.		1600° F.			
				Time	Bend	Time	Bend	Time	Bend	Time	Bend	Time	Bend	Time	Bend	Time	Bend		
1	Regular.....	1900 2100	none none	65 65	OK OK	40 40	• •	18 40	• •	40 40	• •	40 65	• OK	40 65	• OK	40 65	• OK		
2	High chrome.....	1900 2100	24 24	420 420	OK OK	210 90	• •	420 420	OK OK	420 420	OK OK	420 420	OK OK	420 420	OK OK	420 420	OK OK		
3	Low tungsten.....	1900 2100	5 2	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK				
4	Medium tungsten.....	1900 2100	7 4	400 400	OK OK	400 400	OK OK	400 240	• •	400 240	• •	400 400	• OK	400 400	OK OK				
5	High tungsten.....	1900 2100	2 7	210 210	OK OK	210 210	OK OK	210 210	OK OK	210 210	• •	210 210	OK •	210 210	OK OK	210 210	OK OK		
6	High tungsten.....	1900 2100	5 5	210 210	OK OK	210 210	OK OK	210 115	• •	210 115	• •	210 115	OK •	210 210	OK OK	210 165	OK •		
7	Low molybdenum.....	1900 2100	none none	90 90	OK OK	90 40	• •	18 18	• •	40 40	• •	65 90	• OK	90 90	• OK	90 90	• OK		
8	Medium molybdenum.....	1900 2100	none none	90 90	OK OK	90 40	• •	40 40	• •	40 40	• •	90 90	• OK	90 90	• OK	90 90	• OK		
9	High molybdenum.....	1900 2100	23 29	760 760	OK OK	760 760	OK OK	760 760	OK •	760 760	• •	760 760	OK OK	760 760	OK OK	760 760	OK OK		
10	High molybdenum.....	1900 2100	13 14	760 760	OK OK	760 760	OK OK	760 610	OK •	760 115	• •	760 760	OK •	760 760	OK OK	760 760	OK OK		

TABLE 2. (Continued)

Steel No.	Modification	Quench. Temp.	Magnetic Susceptibility	Reheating Temperature															
				1000° F.		1100° F.		1200° F.		1300° F.		1400° F.		1500° F.		1600° F.			
				Time	Bend	Time	Bend	Time	Bend	Time	Bend	Time	Bend	Time	Bend	Time	Bend		
11	High silicon.....	1900 2100	145 129	970 970	OK OK	970 970	OK OK	970 970	OK OK	970 970	OK OK	970 970	OK OK	970 970	OK OK	970 970	OK OK		
12	Titanium.....	1900 2100	none none	420 420	OK OK	420 420	OK OK	420 420	OK OK	420 420	OK OK	420 420	OK OK	420 420	OK OK	420 420	OK OK		
13	High chrome-titanium.....	1900 2100	88 116	420 420	OK OK	420 420	OK OK	420 420	OK OK	420 420	OK OK	420 420	OK OK	420 420	OK OK	420 420	OK OK		
14	Low vanadium.....	1900 2100	none none	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK		
15	High vanadium.....	1900 2100	16 8	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK		
16	High chromium, low vanadium.....	1900 2100	23 19	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK	400 400	OK OK		

^a Number under time column indicates number of hours in Strauss solution before bend test.

^b Very slightly cracked

^c Slightly cracked.

^d Badly cracked.

^e Very badly cracked.

^f Broke.

for about one month, and one for about one and one-half months. All samples were then subjected to the bending test described above and the degree of cracking at the bend noted as a measure of intergranular attack.

Table 2 shows the results of these tests. It also shows the magnetic susceptibility of these steels in the as-quenched condition as measured by the magnetic balance. In judging the comparative resistance to intergranular attack shown by the steels in this table, two factors should be considered; namely, the range of reheating temperature over which attack is found, and the degree of attack after a given time in Strauss solution. The results of these tests can be summarized as follows:

Effects of Addition Elements

Chromium.—High chromium alone makes the steel magnetic and highly resistant to attack except after a reheating at 1100° F.

Tungsten.—Tungsten, in addition to slightly higher chromium than usual, makes the steel slightly magnetic and appreciably improves its resistance to intergranular attack. It will be noted that increasing tungsten does not appreciably increase the magnetic phase in these steels, nor does increasing tungsten increase the resistance to intergranular corrosion. Indeed, the reverse seems to be true in that the 0.08 C, 0.80 W alloy is fully resistant under all conditions, whereas the 0.09 C, 1.21 W alloy is much less resistant, and the 0.10 C, 4.02 W alloy is even less resistant. The implication from these results is that either the slight differences in carbon are accountable for these differences in resistance or that the beneficial effect of tungsten decreases with increasing amounts.

Molybdenum.—With the usual chromium, additions of molybdenum up to 1.87 per cent do not make the steel magnetic nor improve the resistance. With higher chromium and about 3.3 Mo, the steel is magnetic and highly resistant. Even the 0.17 C steel could be considered commercially resistant when quenched from 1900° F., although it is much less resistant when quenched from 2100° F.

Vanadium.—The addition of 0.7 V to a steel with 19.3 Cr leaves the steel nonmagnetic but somewhat improves its resistance. About the same amount of vanadium added to a steel with 22.0 Cr results in a magnetic steel of much greater resistance. The addition of 1.88 V to a steel with 19.1 Cr makes the steel magnetic and fully resistant to attack.

Silicon.—The addition of 3.9 Si to a steel with 20.8 Cr makes the steel highly magnetic and completely resistant to attack under all conditions of testing, even after 970 hr. in the Strauss solution.

Titanium.—The addition of 0.70 Ti to the usual analysis does not make the steel magnetic but makes it fully resistant to attack. When the chromium is high the steel is very magnetic with about the same addition of titanium, and is thoroughly resistant.

Effects of Quenching Temperature and Reheating Temperature

These results also show that in most of the steels, especially in the steels which are partially resistant, the samples quenched from 1900° F. are less susceptible to attack than the samples quenched from 2100°. Similar results on the effect of quenching temperature were reported by Newell. The results further show that in steels which are not resistant, attack is found over the entire range of heating temperatures from 1100° to 1600°, with a maximum effect at 1200° to 1300°. In the steels that were somewhat resistant, the attack is confined to a narrow range of temperature, mainly from 1200° to 1400°. The high-chromium steel, No. 2, shows pronounced failure after the 1100° heating but is totally resistant at all other temperatures.

Steels with higher chromium and nickel content than those just mentioned show a similar increase in resistance when the composition is such that the steel will contain ferrite when quickly cooled from the usual annealing temperatures. The analyses in Table 3 illustrate this feature. Steel 18 differs from steel 17 to only a small extent in silicon and chromium content, yet steel 18 is magnetic and extremely resistant to intergranular attack whereas 17 is nonmagnetic and is susceptible to attack. Again, steels 19 and 20 are fairly close in analysis, yet 19 is not magnetic and is fairly rapidly attacked, whereas 20 is magnetic and highly resistant. Steel 21 is only slightly magnetic and although it is not completely resistant it is more resistant than steel 19. Steel 22 is not magnetic and not resistant and is included to show that high silicon alone is not responsible for the added resistance of some of these alloys.

TABLE 3.—*Analysis of Steels of Varying Resistance to Intergranular Attack*

Steel	C, Per Cent	Si, Per Cent	Ni, Per Cent	Cr, Per Cent	Resistance to Attack
17	0.21	2.27	11.35	23.06	Not resistant
18	0.20	2.69	11.24	23.68	Extremely resistant
19	0.11	1.49	20.81	24.95	Rapidly attacked
20	0.10	2.42	19.64	23.35	Highly resistant
21	0.10	1.92	15.06	23.10	Not completely resistant but more so than 19
22	0.15	2.87	24.70	17.98	Not resistant

In order to determine the practical value of these tests, gas welds were made on annealed samples of steels 9, 10, 11 and 18 and samples were tested in the as-welded condition without subsequent treatment. One set of samples was exposed to boiling Strauss solution for 720 hr. without sign of failure. Another set of samples was exposed to a solution of 10 per cent sulfuric acid plus 0.2 per cent copper sulfate at a

TABLE 4.—General Corrosion Tests

Alloys	Solutions	Loss, Grams per Square Inch				
		2100° F. Quench. No Reheat	2100° F. Quench. Reheat at 1000°, ½ Hr.	2100° F. Quench. Reheat at 1200°, ½ Hr.	2100° F. Quench. Reheat at 1400°, ½ Hr.	2100° F. Quench. Reheat at 1600°, ½ Hr.
0.10 C, regular 18-8..... Subject to intergranular attack	1 per cent boiling H ₂ SO ₄ for 2 hr.	0.053	0.048	0.074	0.056	0.051
	0.5 per cent HCl at room temp. for 96 hr.	0.0100	0.0109	0.0116	0.0108	0.0123
0.09 C, 18-8 with titanium..... Resistant to intergranular attack	1 per cent boiling H ₂ SO ₄ for 2 hr.	0.053	0.050	0.105	0.097	0.087
	0.5 per cent HCl at room temp. for 96 hr.	0.0079	0.0076	0.016	0.016	0.0083
0.09 C, 18-8 with high silicon..... Resistant to intergranular attack	1 per cent boiling H ₂ SO ₄ for 2 hr.	0.050	0.119	0.283	0.211	0.138
	0.5 per cent HCl at room temp. for 96 hr.	0.0052	0.0060	0.025	0.016	0.011
0.10 C, 18-8 with high molybdenum..... Resistant to intergranular attack	1 per cent boiling H ₂ SO ₄ for 2 hr.	0.0043	0.0036	0.047	0.0016	0.0075
	5 per cent HCl at room temp. for 24 hr.	0.092	0.138	0.119	0.100	0.113
0.12 C, 18-8 with high vanadium..... Resistant to intergranular attack	1 per cent boiling H ₂ SO ₄ for 2 hr.	0.115	0.113	0.271	0.308	0.115
	5 per cent HCl at room temp. for 24 hr.	0.023	0.020	0.043	0.017	0.019

temperature of 175° F. for approximately one month, and again there was no sign of failure on any of the welded samples. The latter test closely approximates pickling conditions for nickel silver or brass, the 0.2 per cent copper sulfate acting as an inhibitor to prevent attack on the steel. Welded samples of regular 18-8 alloy not annealed after welding were found to show disintegration near the weld in less than 200 hr. in the Strauss solution.

General Corrosion Tests

In order to establish whether resistance to intergranular corrosion implies resistance to general corrosion when the steel is reheated after annealing, samples of some of these steels were quenched in water from 2100° F. then reheated for $\frac{1}{2}$ hr. at temperature at 1000°, 1200°, 1400°

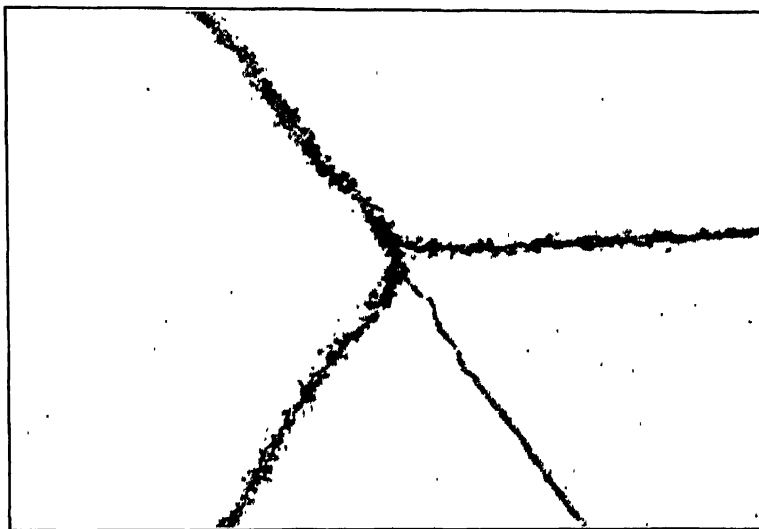
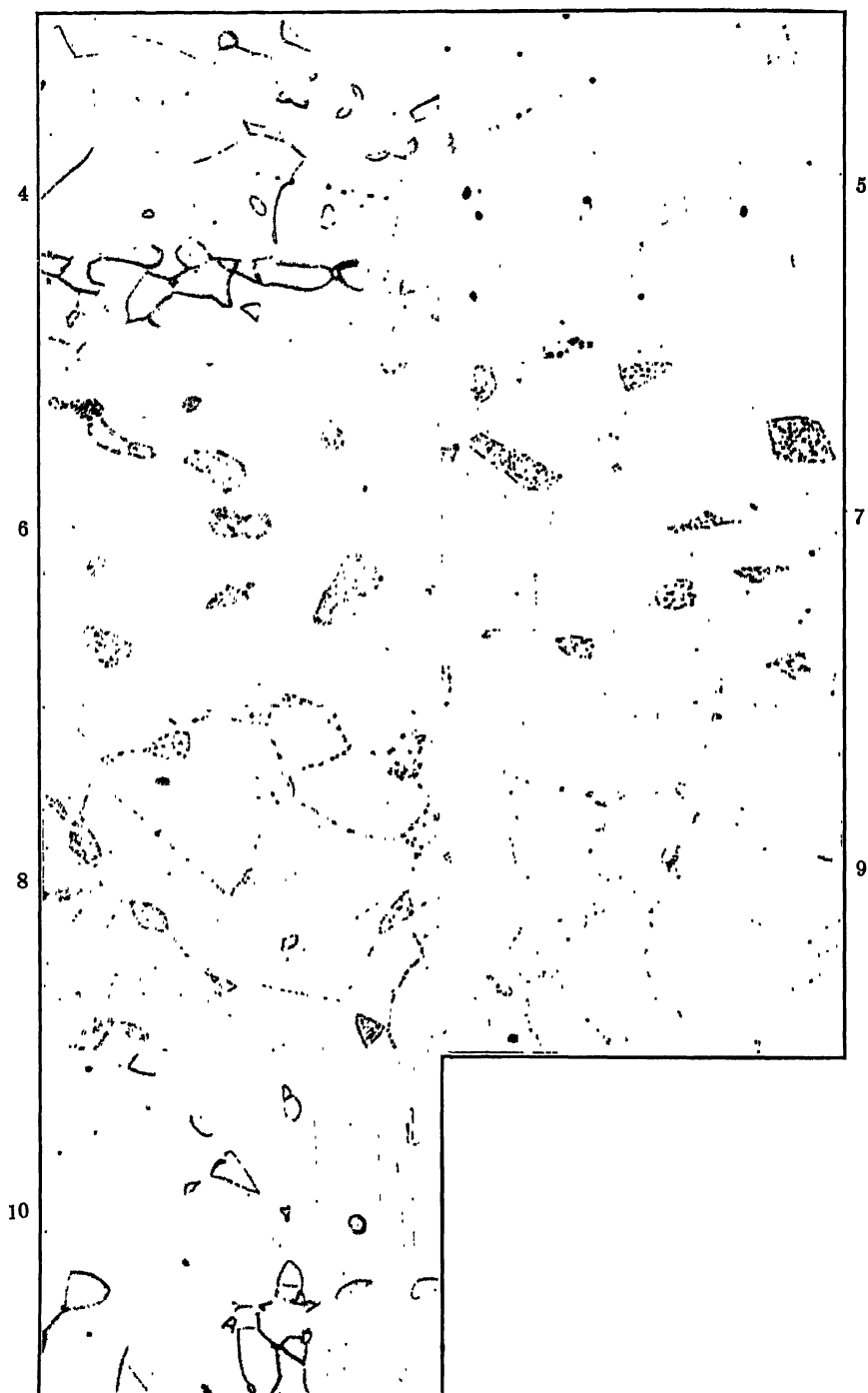
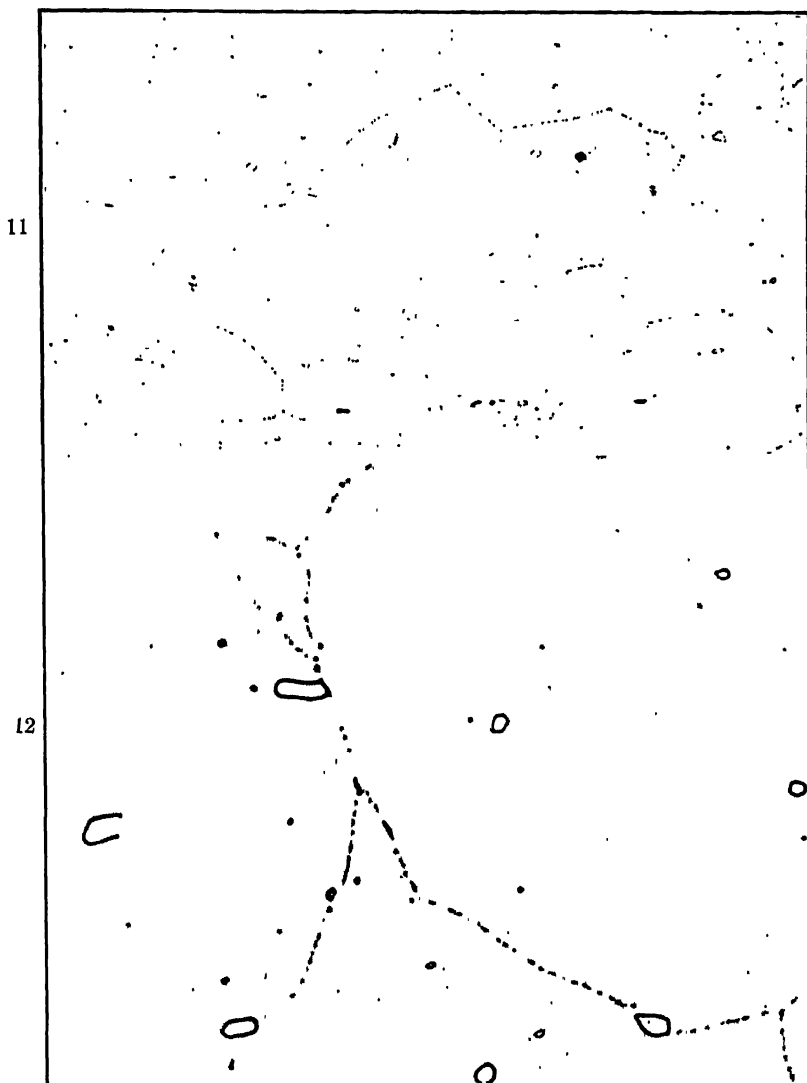


FIG. 3.—REGULAR 18-8 ALLOY QUENCHED FROM 2300° F. AND REHEATED AT 1200° FOR 100 HR. ETCHED WITH MARBLE'S REAGENT.

and 1600° F. The as-quenched and reheated samples were tested in two solutions, boiling 1 per cent sulfuric acid for 2 hr. and solutions of 0.5 per cent hydrochloric acid at room temperature for 96 hr., or 5.0 per cent hydrochloric acid at room temperature for 24 hr. The results of these tests are shown in Table 4.

It will be noted that the steels which are resistant to intergranular corrosion are subject to increased loss in over-all corrosion resistance at some temperatures in this reheating range, and that regular 18-8 alloy, which is strongly susceptible to intergranular corrosion, is much less subject to this decreased over-all corrosion resistance than the steels that are resistant to intergranular attack. This decrease in over-all





FIGS. 11 AND 12.—STEEL 17. QUENCHED FROM 2100° F. AND REHEATED AT 1200° F. FOR 70 HR. ETCHED WITH MURAKAMI REAGENT. FIG. 11, $\times 500$; FIG. 12, $\times 2000$.

FIGS. 4-10.—STRUCTURES OF MOLYBDENUM STEEL NO. 23. QUENCHED FROM 2100° F. FIGS. 4 AND 10 ETCHED WITH MARBLE'S REAGENT; FIGS. 5 TO 9, WITH MURAKAMI REAGENT.

Fig. 4, $\times 500$; Figs. 5 to 10, $\times 750$.

Fig. 4.—As quenched.

Fig. 5.—Reheated at 1100° F.

Fig. 6.—Reheated at 1200° F.

Fig. 7.—Reheated at 1500° F.

Fig. 8.—Reheated at 1800° F.

Fig. 9.—Reheated at 1900° F.

Fig. 10.—Reheated at 2000° F.

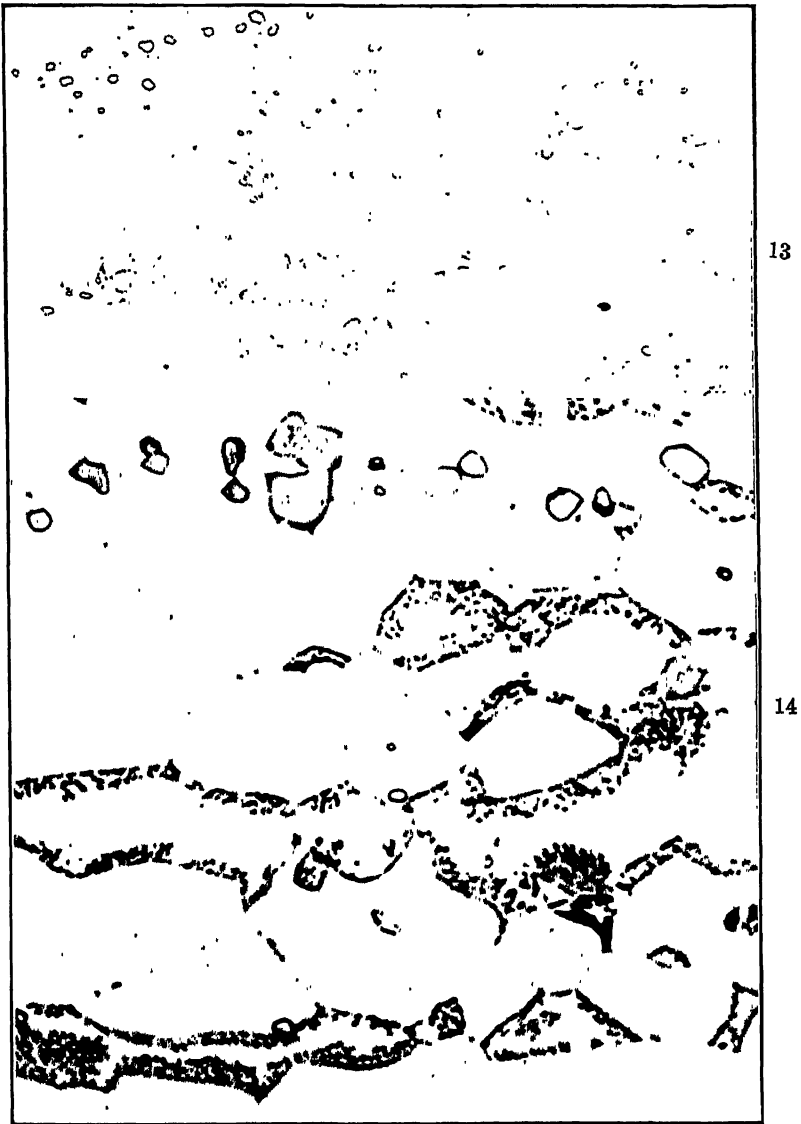
corrosion resistance on reheating the chromium-nickel steels after annealing has been pointed out by other investigators, and it has been implied that it is an indication of susceptibility to intergranular corrosion. The results shown here indicate that lack of resistance to over-all corrosion and lack of resistance to intergranular corrosion are not necessarily due to the same cause. In regard to over-all versus intergranular corrosion, the author fully agrees with Newell's statement: "It is obviously better to have a general diminishing of corrosion resistance with little or no intergranular attack, than to have definite intergranular corrosion which could be construed as making the alloy part quite unreliable under conditions of stress at either low or elevated temperatures. A slight loss representing grain boundary corrosion is much more detrimental than a relatively larger loss in weight representing surface attack."

THE FERRITE HYPOTHESIS

If we assume that precipitation of carbides in a concentrated form along austenite grain boundaries as shown in Fig. 3 is the cause of intergranular corrosion, it should follow, as pointed out by Krivobok, that if we could produce a "matrix which would resist migration of carbides to the grain boundaries, and their agglomeration" we should be able to overcome intergranular attack. This condition seems to be satisfied in the chromium-nickel steels by changing the matrix from a single phase, austenite, to two phases, austenite plus ferrite, the ferrite being other than that possibly resulting from the decomposition of austenite either by cold work or by heating for a long time at about 1100° to 1300° F. The ferrite is introduced by adding the proper amount of molybdenum, silicon, vanadium, tungsten or other elements which form "loop diagrams" with iron. The proper amount of the added element necessary to form ferrite depends on the chromium and nickel content of the alloy; the higher the chromium, the smaller the amount necessary, and the higher the nickel, the larger the amount necessary. In the special alloys made up for this investigation, the chromium was kept on the high side of the 18-8 specification in order to produce ferrite with a smaller amount of the addition element.

The function of the ferrite in these two-phase alloys in regard to prevention of intergranular corrosion seems to be to provide a place for carbides to precipitate other than in a concentrated form along austenite grain boundaries. Figs. 4 to 15 illustrate this point. For determination of carbide distribution, the familiar Murakami reagent was used. For development of the general structure of these steels, the microsections were etched with Marble's reagent, which consists of a 50 per cent hydrochloric acid solution to which about 10 g. of copper sulfate is added per 100 c.c. of solution. This solution is used cold and requires from 1 to 10 sec. for etching the chromium-nickel corrosion-resistant steels. It

is the best etching reagent, although not always highly satisfactory, for the two-phase steels, in that it satisfactorily etches the austenite without overetching the ferrite.



FIGS. 13 AND 14.—STEEL 18. TREATMENT AND MAGNIFICATIONS AS IN FIGS. 11 AND 12

Figs. 4 to 9 illustrate the structural changes which take place in a high-molybdenum 18-8 alloy of the analysis of steel 23, as follows: C, 0.16 per cent; Si, 0.37; Ni, 6.97; Cr, 18.71; Mo, 2.77.

Fig. 4 shows the steel in the annealed condition. Some interesting changes take place in the matrix when the annealed material is reheated, but for the present we will consider only the precipitation of the carbides, which is shown best with the Murakami etch. The annealed sample and the sample reheated at 1000° for 2 hr. show no carbides with the Murakami etch. The samples reheated for 2 hr. each at 1100° and 1200° (Figs. 5 and 6) show precipitation of carbides only in the ferrite areas.



FIG. 15.—SAME AS FIG. 14. $\times 2000$. ETCHED WITH MARBLE'S REAGENT.

After the 1500° reheat, Fig. 7, some carbides are present along the austenite grain boundaries as well as in the ferrite. The 1800° and 1900° samples, Figs. 8 and 9, show re-resolution of the carbides in the ferrite and agglomeration of the carbides along the austenite grain boundaries. When reheated to 2000° , Fig. 10, the steel shows practically complete re-resolution of the carbides.

Figs. 11 to 15 show the distribution of the carbides in the 23 Cr, 11 Ni steels 17 and 18 after a 2100° water quench and a 70-hr. reheat at 1200° F. It will be remembered that steel 17 was fully austenitic and susceptible to intergranular attack, and steel 18 was magnetic as quenched—that is, contained ferrite—and was resistant to intergranular attack.

The photomicrographs show that both these steels contain "original" carbides, that is, carbides which did not go into solution at 2100°, but in addition steel 17 shows carbides precipitated along austenite grain boundaries and twin lines (Figs. 11 and 12) and steel 18 shows some precipitation along austenite grain boundaries but a greater concentration of the precipitate in the ferrite (Figs. 13 and 14). Fig. 15 seems particularly interesting because the structure in the ferrite area closely resembles the pearlite of plain carbon steels.

It is perhaps startling to find that the ferrite in these steels dissolves an appreciable amount of carbon, since it has been generally assumed that carbon dissolves to a considerable extent only in austenite. However, Bain⁸ showed some time ago that carbides dissolve in ferrite in straight high-chromium steel, and Kinzel⁹ has shown that special alloy

TABLE 5.—*Summary of Tests Showing Association between Amount of Ferrite in Annealed Steel and Resistance to Intergranular Attack*

Steel No.	Modification	Resistance to Intergranular Attack	Amount of Ferrite in Annealed Steel
1	Regular.....	Very poor	None
7	Low molybdenum.....	Very poor	None
8	Medium molybdenum.....	Very poor	None
2	High chromium.....	Poor	Large
14	Low vanadium.....	Poor	None
6	0.16 C, high tungsten.....	Poor	Slight
4	Medium tungsten.....	Fair	Slight
5	0.10 C, high tungsten.....	Fair	Slight
10	0.17 C, high molybdenum.....	High	Fairly large
16	High chromium, low vanadium.....	High	Fairly large
9	0.10 C, high molybdenum.....	High	Large
12	Titanium.....	Very high	None
3	0.08 C, low tungsten.....	Very high	Slight
15	High vanadium.....	Very high	Slight
13	High chrome-titanium.....	Very high	Very large
11	High silicon.....	Very high	Very large

ferritic steels can be carburized. The author has also found that straight 18 to 26 per cent chrome irons which are wholly ferritic show definite precipitation-hardening characteristics when reheated to about 900° F.

The evidence is clear that the ferrite in the two-phase steels dissolves an appreciable amount of carbon, and it seems that in some of these

⁸ E. C. Bain: The Nature of the Alloys of Iron and Chromium. *Trans. Amer. Soc. Steel Treat.* 9.

⁹ A. B. Kinzel: Nondeforming Alpha-Delta Carburizing Steel. *Preprint, Amer. Soc. Steel Treat.* (1931).

steels the ferrite dissolves more carbon than the austenite. It also seems to be a fact, at least in the molybdenum steel, that the carbides precipitate out of the ferrite before precipitation occurs in the austenite.

Going back now to the steels that were tested for resistance to intergranular attack, as shown in Table 2, we may summarize as in Table 5. From this summary it may be seen that the relation between resistance to intergranular corrosion and amount of ferrite in the annealed steels, as determined by magnetic susceptibility, is not quite clear, since steels with very high resistance may contain no ferrite, or only a slight amount, or a large amount. But it does seem clear that steels that contain an appreciable amount of ferrite when annealed are not poorly resistant, excepting the high-chromium steel, No. 2.

TABLE 6.—*Effect of Temperature on Magnetic Susceptibility of Two-phase Steels Measured as Grams-pull on Magnetic Balance*

Steel	Steel 2	Steel 9	Steel 11	Steel 15
	Resistance to Intergranular Attack			
	Poor	High	Very High	Very High
As rolled.....	29	9	172	15
600° F. for 15 hr.....	31	6	174	15
1000° F. for 15 hr.....	25	7	164	14
1100° F. for 15 hr.....	21	5	69	11
1200° F. for 15 hr.....	17	2	35	12
1300° F. for 15 hr.....	16	0	9	10
1400° F. for 15 hr.....	19	0	1	8
1500° F. for 15 hr.....	19	0	1	20
1600° F. for 15 hr.....	20	0	1	19
1700° F. for 10 min.....	21	1	167	17
1800° F. for 10 min.....	20	1	170	16
1900° F. for 10 min.....	24	23	164	13
2000° F. for 10 min.....	25	29	135	9
2100° F. for 10 min.....	24	29	146	7
2200° F. for 10 min.....	34	34	163	12

There is much room for speculation as to why some of these two-phase steels are totally resistant whereas others are somewhat subject to attack. It is possible that the ferrite produced with silicon, for example, has a greater solubility for carbon than the ferrite produced by tungsten. Or it may be that in the steel made ferritic by means of high chromium alone the carbides precipitate out of the austenite before they are precipitated in the ferrite. Since the structures of none of these steels have been studied as thoroughly as those of the molybdenum

steel, No. 23, it is perhaps best to avoid these speculations until the microstructural changes taking place in these steels are better known.

It was thought that in some of the steels the ferrite might be delta iron, or high-temperature ferrite, whereas in other steels the ferrite might be similar to that in the high-chromium irons; that is, it would persist at all temperatures up to the melting point. Some tests were made to determine whether this is true and some very interesting results were obtained on the magnetic balance, as shown in Table 6.

From Table 6 it seems clear that the ferrite in the annealed high-silicon and high-molybdenum steels, 11 and 9, is definitely delta ferrite, since the magnetic susceptibility decreases to a very slight amount at about 1300° to 1400° F. and then returns strongly at higher temperatures. On the other hand, in the annealed high-chromium and high-vanadium steels, 2 and 15, the ferrite persists through the whole range of temperatures although there is a minimum in steel 2 at 1300° and in steel 15 at 1400° F.

These results do not help to establish the relationship between the ferrite and the resistance to intergranular attack, because of the two steels that were found to be completely resistant to intergranular attack one seems to contain high-temperature ferrite and the other low-temperature ferrite, and the same is true of the two steels that were not completely resistant.

Of the addition elements investigated, only titanium seems to be able to produce immunity from intergranular corrosion when added in an amount insufficient to develop the ferrite phase. No explanation of the inhibiting action of small amounts of titanium is at present available. It is known that if carbon is sufficiently low or if the chromium is fairly high, the addition of small amounts of titanium causes the formation of

TABLE 7.—*Effect of Quenching Temperature on Magnetic Change and Susceptibility to Intergranular Attack Developed in Regular 0.09 Per Cent C, 18-8 Alloy by Reheating to 1200° F. for 100 Hours*

Quenching Treatment	Magnetic Susceptibility, Grams-pull after 100 Hr. at 1200° F.	Depth of Penetration, In. after 3 Hr. in Strauss Solution
1700° F. for 2 hr.	13.6	0.0004
1900° F. for 1 hr.	5.6	0.012
2100° F. for 30 min.	2.4	0.015
2300° F. for 15 min.	1.5	0.021

the ferrite phase, and titanium therefore can definitely be included with the other ferrite-forming elements. But until further facts are established, it seems necessary to conclude that the inhibiting action of small amounts

of titanium results from a different cause than that which seems to account for the resistance of the steel when the proper amount of silicon, for example, is added.

On the basis of the foregoing discussion, the following hypothesis may be formulated: The addition of a ferrite-forming element to a chromium-nickel iron alloy which would otherwise be completely austenitic when rapidly cooled from about 1850° to 2100° F., in sufficient amount to develop ferrite in the alloy when rapidly cooled from about 1850° to 2100°, will appreciably increase its resistance to intergranular corrosion. The function of the ferrite in accomplishing this resistance is to provide a place for the carbides to precipitate otherwise than in a concentrated form along austenite grain boundaries. In order to decrease the amount of addition element necessary to produce ferrite, a chromium content higher than 18 per cent may be used.

SUMMARY AND COMMENTS

It has been shown that the chromium-nickel corrosion-resistant steels can be made to contain two phases, austenite and ferrite, by adding elements like silicon and molybdenum, which form "loop diagrams" with iron, and that the two-phase steels are much more resistant to intergranular attack than the single-phase austenitic steels. It has been postulated that the two-phase steels owe their resistance to this type of attack to the precipitation of carbon within the grains of ferrite.

The validity of such a hypothesis depends on the supposition that intergranular attack is caused by precipitation of carbides in a concentrated form along austenite grain boundaries. The fact that the elimination or reduction of such precipitation by the introduction of the ferrite phase increases the resistance to intergranular attack adds strength to this supposition, but the explanation of this type of attack is still not clear. The author would like to point out some facts which appear to contradict the prevailing theories on this subject.

The theory that the magnetic phase resulting from the decomposition of austenite is an important factor in developing susceptibility to intergranular attack does not seem tenable, for several reasons. Although the magnetic phase can be developed in 18-8 alloy by reheating for a long time at about 1200° F., it is not produced by heating for a short time at this temperature, and yet this short-time heating causes susceptibility to intergranular attack. The more stable austenitic steels, like the 18 Cr, 25 Ni steel 22, are subject to intergranular attack although they never develop the magnetic phase on reheating after annealing. In regular 18-8 alloy, the amount of magnetic phase developed by reheating for a long time at 1200° F. depends on the temperature from which the material was last quenched, and Krivobok has shown that, in general, the

higher the quenching temperature before reheating, the lower the amount of magnetic phase after heating for a long time at 1200° F. But Newell showed that the higher the quenching temperature before reheating, the greater the susceptibility to intergranular attack; and the author has found the same thing to be true, as shown in Table 7. For these reasons the author believes that the magnetic phase resulting as a decomposition of austenite may accompany the condition which causes susceptibility to intergranular attack but is not a factor contributory to this condition.

Aborn and Bain have suggested that if carbon were permanently precipitated in some way so that there could be no further precipitation along grain boundaries when the annealed material was reheated, the intergranular attack would be minimized. Such a condition exists partly in the 23 Cr, 11 Ni steel 17, which shows "original" carbides in Figs. 10 and 11. This steel, in spite of its high carbon, was found to be fairly resistant to intergranular attack after reheating for 70 hr. at 1200°, and it was thought that this resistance was due to the fact that, because of the presence of the "original" carbides, there was a decreased amount of carbon available for solution and reprecipitation. However, the presence of permanently precipitated carbides is not alone responsible for the better resistance of this steel, because in the 18 Cr, 25 Ni steel 22, "original" carbides also are present after annealing and yet this steel is only poorly resistant.

The photomicrographs frequently used to point out the cause of intergranular corrosion show structures similar to that of Fig. 3. In such structures carbides are definitely recognized in a concentrated form along grain boundaries, but these structures are developed only after a long time at the reheating temperature. If the steel represented by Fig. 3 had been heated for only 2 min. at 1200° it would become subject to intergranular attack, but the structure could hardly be distinguished from that of the resistant annealed material. The only manifestation of a change in structure would be, possibly, a more rapid etching. Many sections adjacent to welds in regular 18-8 alloy, which were shown by tests in Strauss solution to be subject to intergranular corrosion, have been very carefully examined for structure and for magnetism and no difference other than the corrosive attack has been found between the metal in the sensitive zone and the metal that was thoroughly resistant to attack. It may be argued that if precipitation is visible after 100 hr. heating at 1200° F., some precipitation of the same nature must have occurred after only a very short time of heating at the same temperature. This seems reasonable, and yet migration of carbon and agglomeration of carbides are certainly functions of time at temperature and the carbides which we see at the grain boundaries after 100 hr. of heating may possibly not even have been definitely formed after the very short time at temperature. It is suggested that incipient

precipitation of carbon rather than the definite formation of carbides is the cause of intergranular attack, and it is hoped that X-ray studies will be undertaken to establish the cause of this intergranular attack, since the microscope, at least at magnifications up to 2000 dia., seems to be inadequate.

If the cause of intergranular corrosion is incipient carbon separation from solid solution rather than carbide precipitation, the prevailing idea of chromium impoverishment cannot hold, because chromium cannot be removed until the carbide is formed. But there are other reasons to believe that the chromium-impoverishment idea is not a satisfactory explanation of the phenomenon. For instance, in the tests reported above, considering steels of nearly the same carbon content, steels 11 and 15, with chromium contents of 20.8 and 19.1 per cent, are much more resistant to intergranular attack than steels 2 and 16, with chromium contents of 21.9 and 22.0 per cent. Again, considering the higher type of alloys, steel 20 with 23.35 per cent Cr is much more resistant to intergranular attack than steel 19 with 25.0 per cent Cr.

That decreased corrosion resistance accompanies the condition of incipient carbon separation from solid solution in tool steels, that is, when the quenched steel is tempered to the troostitic condition, is well known, and was pointed out in connection with intergranular corrosion by Kinzel in his discussion of one of the papers by Aborn and Bain mentioned on page 306. In the paper by C. G. Merritt¹⁰ this same phenomenon is shown in the lower type of chromium irons. In a paper now in preparation on the effect of heat treatment on the corrosion resistance of chromium irons it will be shown that this phenomenon is also present in the higher type of chromium irons up to 26 per cent Cr.

It seems reasonable to believe that this decrease of corrosion resistance accompanying incipient carbon separation also occurs in the chromium-nickel steels and that it is the cause of the intergranular attack. However, much work remains to be done before the cause of this intergranular attack is definitely established.

ACKNOWLEDGMENT

The author is grateful to his colleagues in the Research Laboratory of the Crucible Steel Co. of America for the assistance given him in acquiring the data presented here, and to the other metallurgists in the company, particularly Mr. A. A. Hassan, Jr., and Dr. F. H. Allison, Jr., who helpfully discussed with him the subject matter of the paper. Permission to present the data was given by Dr. John A. Mathews, vice president, and to him the author is particularly indebted for kindly advice and constant encouragement.

¹⁰ See page 272.

DISCUSSION

(John A. Mathews presiding)

R. H. ABORN, Kearny, N. J. (written discussion).—Mr. Payson's account of his work and discussion on prevention of intergranular corrosion in 18-8 chromium-nickel steel and similar alloys affords a useful record on what has been done to offset the occasional instability of this alloy under certain high-temperature conditions. The principal conclusion—that the presence of ferrite, in general, reduces susceptibility to intergranular attack—is corroborated by our own investigations of such steels during the past year and one-half. It is gratifying also to find confirmatory evidence of our observations, that ferrite is often apparently fickle in its attentions toward carbon, and that the mere presence of ferrite is no guarantee of nonsusceptibility to intergranular attack, but rather that each type of ferrite stabilizer has its own specific characteristics.

We question, however, the validity of the author's proposed concept of the cause of intergranular attack, which involves discarding the chromium-impoverishment theory—first, from a philosophical point of view, and second from the viewpoint of direct observation. Philosophically, the proposal would lead us into the realm of unprofitable speculation. We cannot but ask the question, at what precise stage does "incipient precipitation" become the definite formation of carbides? The case is no better here than in the purely speculative consideration of age-hardening in which no one has been so bold as to venture a guess as to the precise nature of the ultimate hardening particles. Furthermore, if "incipient carbon separation" is the cause of intergranular attack, is it not inconsistent with the weight of evidence presented on the improvement resulting from the presence of ferrite, since this "incipient carbon separation" is no respecter of phases, and must presumably precede the appearance of visible carbides in ferrite as well.

Actually, however, it seems doubtful whether the conclusions are warranted by the evidence offered. For example, the author reports that a regular 18-8 with 0.09 per cent C, although subject to intergranular attack after only 2 min. at 1200° F., failed to show any evidence of carbides even at a magnification of 2000 dia. We found among our materials a thoroughly homogenized 18-8 alloy of substantially identical composition. After a similar treatment at 1200° F. it also was found susceptible to intergranular attack, but the microscopic evidence was unequivocal. At a magnification of 1200 dia. definite particles (presumably carbides) were visible along the grain boundaries, having the same general microscopic characteristics as those shown in Fig. 3, the essential difference being that in the former case they were relatively few, and the severity of the attack was correspondingly lessened.

If this microscopic appearance indicates incipient carbide precipitation it would appear to us that it entails removal of effective chromium from solid solution just as surely as though the particles were very large. Clearly no one can entertain the thought of elemental carbon (graphite) precipitation in an alloy carrying 18 per cent Cr. Further support of the chromium-impoverishment concept is to be found in the change of electrochemical potential to a value corresponding to lower chromium content.¹¹ Again, it would seem unwise to discard the chromium-impoverishment mechanism merely on the basis of relative amounts of chromium present, without regard to modifying influences such as a change in the relative amounts of other elements present or in the previous history of the specimen.

¹¹ B. Strauss, H. Schottky and J. Hinnüber: Carbide Precipitation during Tempering of Corrosion-resistant Nonmagnetic Chromium-Nickel Steel. *Ztsch. f. anorg. u. allg. Chem.* (1930) 188, 309.

In all our experience with nearly 1000 specimens of such steels exposed to carbide precipitation temperatures for periods ranging from a few seconds to thousands of hours, we have yet to find a single occurrence of intergranular attack without definite characteristic grain boundary alteration and evidence of particle precipitation.

Finally, the evidence we have from our own and other laboratory work confirms Mr. Payson's statement that an appropriate amount of titanium (the percentage depending upon the carbon content) renders this alloy fully resistant to intergranular attack. The ability of titanium to produce a stabilized alloy without the accompaniment of ferrite is noteworthy in that it provides a means of retaining unaltered all of the valuable physical and mechanical properties of the original austenite. The explanation of the action of titanium becomes relatively simple from the viewpoint of the chromium-impoverishment concept as it involves substantially the formation of titanium carbide instead of chromium carbide, thereby avoiding chromium depletion. Such alloys stabilized with titanium have been used abroad for some time with good results; they may now be obtained from various subsidiaries of the United States Steel Corp. and from others operating under the Krupp patents.

J. A. MATHEWS, New York, N. Y. (written discussion).—There can be little doubt that the tendency to intergranular corrosion in austenitic chromium-nickel corrosion-resistant steels has been the chief retarding influence in limiting their use for chemical plant and similar structures where the welding process is involved and where size limitations prevent the possibility of heat treatment after welding. Much work has been done as regards the cause of this phenomenon but Mr. Payson's paper deals primarily with its cure.

Most of us can recall receiving a gift at some time that raised the question in our minds, "what are we going to do with that"? For the past several years we have been hearing more or less about delta iron. Some of us know where to look for it on the iron-carbon equilibrium diagram; some of us have seen it under the microscope and some of us have looked at it without knowing what it was. Mr. Payson's paper seems to be the first instance in which anyone has tried to answer the question, "what are we going to do with it"?

X-ray experts tell us that delta iron and alpha iron are identical in atomic arrangement, yet they differ in genesis and may differ in function. In the Howe Memorial Lecture in 1925, I outlined in a somewhat popular way what the general public knows about steel—it is magnetic; it rusts and some of it can be hardened.¹² This I described as alpha iron metallurgy. I then described the outstanding characteristics of austenitic steels—they do not rust; they are nonmagnetic and they soften by quenching rather than harden. This I described as gamma iron metallurgy, and stated that "we shall know better how to use these steels when we understand their metallurgy and properties."

It is hard to believe that only seven years ago we thought that the metallurgy of austenitic steels was simplicity itself as compared with ordinary steels. The evidence of the last seven years has disabused our minds on this score. Now Mr. Payson proposes to add delta iron metallurgy as something that may prove of great value when it is better understood.

The elements that Mr. Payson has employed to bring about high resistance to intergranular attack have been employed by others in some instances, with more or less satisfactory results, but no one so far as I know has connected their presence with their ability to produce a certain amount of delta ferrite; in fact, it is a question of balancing the entire composition to produce this result rather than merely adding a new element to chromium-nickel corrosion-resistant steel.

¹² J. A. Mathews: Austenite and Austenitic Steels. *Trans. A.I.M.E.* (1925) 71, 568.

It is too early to say what the practical importance of this work may be but I anticipate that it will be very great and at any rate the paper is an important contribution to a subject that is of most vital importance to the chemical industry. Much work remains to be done to establish exact limits of composition which give maximum resistance to intergranular corrosion. It must also be borne in mind that some of these steels may not be fabricated readily in all forms for which they may be required; also that they will represent a considerable difference in cost and the specific influence of the special added element must be taken into consideration in connection with each commercial application.

A. B. KINZEL and R. FRANKS, New York, N. Y. (written discussion).—The work reported by Mr. Payson is most timely, as one of the major problems in connection with corrosion-resistant austenitic steel pertains to the retention of satisfactory physical and chemical properties in the as-welded condition. Mr. Payson has not only covered this problem thoroughly but has contributed toward a better understanding of the phenomena involved.

While intergranular corrosion in connection with welding is important, many of us have come to consider the problem as a whole from the standpoint of long-time service at temperature, as in superheater tubes, oil stills and the like. Because of this some of the terms used by the author, while entirely correct and consistent, are apt to be misinterpreted. Throughout the work the terms "highly resistant" and "fully resistant" to intergranular corrosion are used. The author has in mind, of course, intergranular corrosion produced by welding. Mr. Payson's tests, which consist in heating at temperature for 10 min. or $\frac{1}{2}$ hr., while entirely justified when welding is the major consideration, are not applicable if long-time high-temperature service is involved. The use of long periods of test in the copper-sulfide solution, however, has been carried out in a most satisfactory manner.

The use of the magnetic balance as devised by Mr. Payson is most ingenious and certainly tends to shed light on the whole matter, even though the results frequently are complicated by the two kinds of magnetism so well pointed out by Mr. Payson.

While we can check most of the experimental results and statements made by the author, there are a few that are surprising; for example, 0.08 per cent C, 0.80 per cent W is stated (p. 314) to be fully resistant under all conditions, an experimental result which we cannot check. Again, in Table 3, minor differences in analysis are shown to have a most marked effect on magnetic properties. It would certainly appear that some other factor has affected these results, although this would not affect the major conclusion drawn from Table 3, which seems to be justified; namely, the more magnetic materials are more resistant than the lesser magnetic materials.

We too can check the general observation that in most of these alloys the over-all corrosion resistance decreases as the resistance to intergranular corrosion increases, but do not believe that this is an important element in the ferrite hypothesis presented by the author. The photographs are most striking and present in themselves a complete and continuous story. However, even with the weight of these, there is still much left to be explained on the basis of the ferrite hypothesis. It seems to us that the major influence of ferrite is to limit the continuity of the austenite grain boundaries and in this way inhibit the propagation of intergranular notches on testing after attack has taken place. The carbide solution phase of the ferrite hypothesis seems to us to be very much in doubt. High-temperature ferrite undoubtedly does dissolve an appreciable amount of carbon, but we fail to see any evidence that it dissolves more carbon or even as much carbon as the austenite. It is understandable that the carbides may precipitate from the ferrite before precipitating from the austenite. This is a function of the shape of the solubility curve and not of the total amount of carbon dissolved in the ferrite or austenite.

Mr. Payson has very well shown that many of the present theories, particularly the chromium-impoverishment theory, leave much to be explained, and very properly states that the ferrite hypothesis is also incomplete. Without wishing to enter into a controversy regarding a satisfactory theory, we might say that in our opinion the troostite hypothesis which we have previously presented, and which is referred to in the paper, seems to be the most satisfying at the present time.

The paper has been written with a particularly open mind. The ferrite hypothesis has been given without any claim that it is sufficient. Data both for and against it have been presented, and Mr. Payson is to be highly congratulated on an unbiased discussion which is a real contribution to our technical knowledge.

P. PAYSON (written discussion).—The author takes this opportunity to correct the impression he may have given that the acid copper sulfate testing solution was originated by Dr. Benno Strauss and his coworkers. Since the presentation of the paper, it has been brought to the attention of the author that this testing solution was developed at the Brown-Firth Research Laboratories under Dr. W. H. Hatfield. The solution has been associated with Dr. Strauss because he was probably the first to suggest its use in this country.

The discussion by Dr. Mathews is deeply appreciated, and the author will indeed be proud if he can attain in delta iron metallurgy, even in a small way, the success which Dr. Mathews has had in alpha and gamma iron metallurgy.

Messrs. Kinzel and Franks point out that tests after short time reheating, as reported in the paper, cover only part of the problem of resistance to intergranular corrosion. But there are not many applications in which parts are exposed to long heatings at 1100° to 1600° F. and subsequently subjected to active electrolytes. Long-time heating at these temperatures may involve changes in mechanical properties, or changes due to oxidation or sulfurization, but these are aside from the question under discussion. The author had occasion, recently, to examine thoroughly a Rezistal 2-C part which had given perfect service for 18 months at temperatures between 1000° and 1650° F., with occasional shutdowns during which the part was allowed to cool to atmospheric temperature. This was a 0.18 per cent C steel, and yet no trace of intergranular attack was found. The obvious explanation is that, even though the steel in this condition would be readily susceptible to intergranular attack if subjected to active electrolytes, the service at these elevated temperatures precluded the presence of active electrolytes.

The author has retested by two independent methods, including the electrical resistance method of Rutherford and Aborn, the 0.08 C, 0.80 W steel, the perfect resistance of which Messrs. Kinzel and Franks were not able to check, and has found that it is entirely immune to attack. Apparently minor differences in analyses may produce important differences in resistance to intergranular attack, and the steel tested by Kinzel and Franks may not have been identical with that tested by the author.

The author cannot agree with Kinzel and Franks' interpretation of the function of ferrite in developing resistance to intergranular attack. The ferrite is invariably strung out in the direction of rolling and therefore cannot effectively limit the continuity of the austenite grain boundaries. Furthermore, in the completely resistant two-phase steels where there may be several layers of austenite grains at the surface without any interfering ferrite grains, carefully polished microsections show no trace of intergranular attack after long-time exposure to the acid copper sulfate solution. Again, if the ferrite acted merely to limit the continuity of the austenite grain boundaries, all two-phase steels would have resistance more or less proportional to the amount of ferrite, regardless of the addition elements used to develop the ferrite,

but admittedly this is not so, since steel 2 has more ferrite than steel 15, yet steel 15 is much more resistant.

In regard to Dr. Aborn's discussion, the author was led to propose the idea of incipient carbon separation because he was unable to recognize definite carbides in samples that were reheated for very short times and yet were susceptible to attack in the acid copper sulfate solution. The author confesses a lack of admiration for this idea because it is practically impossible to prove experimentally, and he is glad to have the precedent of the "knot" theory presented by Dr. Merica¹³ in explanation of age hardening. In many alloys, age-hardening characteristics are found before the presence of definite compounds can be detected, and Dr. Merica argues that these characteristics are due to a transition phase between the solid solution and the definite compound. In the same way the author feels that intergranular attack may be due to a transition phase between carbon in solid solution and carbon in a definite carbide.

It is unfortunate that Dr. Aborn and the author disagree as to whether or not carbides are actually present at the grain boundaries after short-time heating. The satisfactory preparation of microsections of 18-8 is admittedly difficult. There is no doubt that the sample reheated for a short time etches much more rapidly at the grain boundaries than the annealed sample, and that frequently the grain boundary condition in the reheated sample looks like carbide precipitation. But the author is convinced that unless the Murakami reagent etches the austenite grain boundaries, there are no carbides present, and he has frequently found, in samples that were susceptible to attack, that the Murakami reagent did not etch the austenite grain boundaries. It seems reasonable therefore that the attack is due to something other than carbide precipitation.

The fact that proper additions of titanium prevent susceptibility to intergranular attack no more proves the validity of the chromium-impoverishment theory than does the fact that very low-carbon steels are resistant. The formation of insoluble titanium compounds containing carbon actually removes carbon from any possible reactions in the steel, and the steel behaves like one having a carbon content equal to the balance of the carbon not permanently combined with titanium. If this balance is greater than about 0.07 C, the steel will be susceptible to attack in spite of the titanium in the analysis, unless the steel is of a two-phase composition.

¹³ P. D. Merica: The Age-hardening of Metals. *Trans. A. I. M. E.* (1932) 99, 13.

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